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# MATHEMATICAL MODELING OF EMISSIONS FROM COOLING TOWERS USING COAL GASIFICATION WASTEWATER

D. A. Green
K. E. Leese
W. J. McMichael

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, North Carolina 27709

EPA Project Officer: N. Dean Smith
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U. S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Office of Research and Development
Research Triangle Park, North Carolina 27711

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and

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The report describes a computer program that calculates atmospheric emissions from counterflow cooling towers when using pretreated coal gasification wastewaters as tower makeup water. Air stripping and biological oxidation are both incorporated into the mathematical model as possible contaminant removal mechanisms. Confirmation of model predictions was demonstrated by a 30-cm square by 91-cm high laboratory cooling tower using both simulated and real pretreated coal gasification wastewaters. Stripping of volatile components was shown to be the primary contaminant removal mechanism. Cycles-of-concentration (i.e., the ratio of makeup water flowrate to blowdown flowrate) is the major tower operating parameter influencing the amount of volatile contaminants remaining in the blowdown.

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| Mathematical Models | Stationary Sources | 12A |
| Cooling Towers | Biological Oxidation | 13A, 07A, 13I |
| Coal Gasification | Air Stripping | 13H |
| Waste Water | | |
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## ABSTRACT

A computer program is developed which calculates atmospheric emissions from counterflow cooling towers when using pre-treated coal gasification wastewaters as tower makeup water. Air stripping and biological oxidation are both incorporated into the mathematical model as possible contaminant removal mechanisms. Confirmation of model predictions is demonstrated by means of a 30-cm square by 91-cm high laboratory cooling tower using both simulated and real pre-treated coal gasification wastewaters. Stripping of volatile components is shown to be the primary contaminant removal mechanism. Cycles of concentration (i.e., the ratio of makeup water flowrate to blowdown flowrate) is the major tower operating parameter influencing the amount of volatile contaminants remaining in the blowdown.

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# CONVERSION FACTORS

| To Obtain | Multipy | By |
|---|---|---|
| Grams | pounds | 453.6 |
| Liters | $Ft^3$ | 28.32 |
| Centimeters | Feet | 30.48 |
| Joules | Btu | 1055. |
| Atmospheres | psi | 0.06805 |
| $g/cm^2 min$ | $pound/ft^2$ hr | 0.008143 |

°C = (°F - 32) x .5555

°F = (°C x 1.8) + 32

# 1.0 INTRODUCTION

There is substantial incentive on the part of synfuels developers to incorporate maximum recycle and reuse of wastewaters into the design of new synfuels production facilities. The incentive for "zero liquid discharge" arises from (1) expectation of regulatory restrictions on discharge of treated effluents, and (2) conservation of water resources. Many proposed synfuels facilities have indicated the choice of zero liquid discharge schemes in their plant designs. Several projects proposed to the U.S. Synthetic Fuels Corporation also contain zero discharge schemes.

One approach to accomplishing zero liquid discharge involves the reuse of process condensates as cooling tower makeup water. However, synfuel condensates often contain both inorganic and organic impurities. These contaminants have been known to cause both operational and environmental problems in cooling tower operation in some cases.

## 1.1. The Use of Wastewater in Cooling Towers

In one plan (Milios, 1975) to use cooling towers to treat water from zero liquid discharge coal gasification plants, it was calculated that 67 percent of the wastewater would be returned to the atmosphere as water vapor through evaporation, 24 percent would be consumed by the steam-carbon reaction, 2.5 percent would be present in the ammonia by-product; the remainder would be associated primarily with the solid waste products.

Gloyna (1970), described a program of water management which used cooling towers for concentrating refinery wastewater. It was found that phenol and phenolic compounds were removed from the wastewater. Although the relative importance of mechanisms for removal of organic materials were not determined, the mechanisms were thought to involve a combination of biodegradation, precipitation, absorption, and stripping. In one year of cooling tower operation, the only blowdown was the removal of sludges from the bottom of the tower. The sludge that was produced in the bottom of the cooling tower resisted aerobic digestion and contained a high concentration of heavy metals. The fouling of heat exchangers and cooling tower equipment as a result of growth of microorganisms did not occur, and it was postulated that the abnormally large amounts of heavy metals in the circulating water inhibited the growth of microorganisms. The cooling tower thus served as a wastewater treatment process, with an oily sludge as the only liquid effluent from the process.

Fleishman (1975) described the biological oxidation of phenol in a cooling tower at Sun Oil's Toledo refinery. Sodium hexametaphosphate was used as a corrosion inhibitor and a microbial nutrient for biological oxidation. Due to the biological oxidation in the cooling tower, the dissolved oxygen concentration in the cooling water was less than 2 ppm. No biocides were used in the cooling tower. Fouling and/or corrosion of the heat transfer surfaces occurred when phenol concentrations in the circulating cooling water were greater than 5 mg/L. At the Toledo refinery, the heat exchangers were backflushed daily. Harpel and James (1973) show examples of chemical plant wastewaters treated in cooling towers and indicate that most of the organic matter (mainly benzene and toluene) vaporized over the tower at 3 and 4 cycles of concentration.

In addition to the proposed use of industrial wastewater as cooling tower makeup, treated municipal wastewater has also been considered for use in cooling towers and some of the consequences of this practice were reported (James, et al., 1976). Even after biological oxidation, sewage is highly nutrient-rich. This results in slime and algae growths which cause serious operational problems when using municipal wastewater in a cooling tower. Disinfection by chlorination and frequent shock treatment was considered normally adequate to prevent operating problems due to biological growth. Biological treatment with high phosphate removal was recommended for consideration. Water with a high silica content required lime treatment whether or not phosphate was removed, but the treatment could be easier if the approved biological treatment was used (James, et al., 1976).

In a water reuse study sponsored by the petroleum industry, Grutsch and Griffin (1978) report that, even at 6 or more cycles of concentration in a refinery cooling tower, the residual ammonia in recirculating cooling water is typically about equal to or less than the ammonia content of the makeup water. Similarly, Grutsch and Griffin, (1978) reported 80 percent removal of phenol and 50 percent removal of TOC in a cooling tower fed with treated refinery sour water where no biological activity occurred. To verify the mechanisms of ammonia and organic removal, additional tests were run under both slightly alkaline and acidic pH conditions after sterilizing the recycle water with a copper biocide. The test results after sterilizing the systems were no different than those obtained previously. Therefore, it was concluded that biological oxidation was not an important removal mechanism for ammonia and organics in the cooling tower. In addition, the rate of removal of phenolics was approximately the same at slightly acidic and alkaline conditions. It was concluded in this study that, since air stripping was the predominant contaminant removal mechanism, an effective treatment of refinery wastewater makeup would usually be necessary to control atmospheric emissions from cooling towers.

In a similar study by the Georgia Kraft Company (1971), evaluations of biological action in a laboratory cooling tower were made. Two identical cooling towers were constructed with one tower operating on air-stripping alone and the other being seeded with bacteria and fed with nutrients to operate with both air-stripping and biological action. Experiments were performed when the biological growth had covered the tower packing surface to the extent that portions of the biological growth would slough off and fall to the holding basin. Biological action contributed only 4 to 12 percent more BOD reduction than did stripping alone. The extent of biological action was dependent upon the flow rates of liquid and gas and appeared to increase with increasing liquid-to-gas ratio. Biological action in conjunction with stripping produced greater BOD removal since the biological reactions could attack the nonvolatile portion of the BOD-producing compounds. It was concluded that the amount of increased BOD removal due to biological action did not appear to justify the added operational costs due to solids control.

In a study by James, et al (1976) to determine the feasibility of wastewater treatment in cooling towers, the microorganisms in a cooling tower were projected to remove 90 percent or more of the phenols and reduce effluent organic carbon and oxygen demand from refinery sour water stripper bottoms; no mass balance data were given to support this projection. This mechanism was reportedly inhibited by sulfide because the sulfides apparently killed the phenol-oxidizer microorganisms. Therefore, it was recommended that when sulfide levels exceed 2 mg/L in the wastewater, the water should be diverted from the cooling system (James, et al., 1976).

A few studies have sought to encourage bioactivity in the tower to accomplish simultaneous cooling and water treatment. Most of these studies, however, fail to provide convincing evidence of significant contaminant removal by chemical or biological activity. The best documented study of the successful operation of such practice is probably that by the Sun Oil Company refinery in Toledo, Ohio, using refinery wastewater. Phenol, COD, and TOC removals were found to be 99.4 percent to 99.9 percent, 62 percent to 93 percent, and 67 percent respectively (Mohler and Clere, 1973). Another study using stripped refinery sour water gave 92.0 percent to 97.2 percent removal of phenolics (Hart 1973), while a third study using secondary sewage effluent showed BOD and COD removals of 77 percent and 80 percent, respectively (Petrey, 1973). McGuire and Dishinger (1984) found that certain disinfection techniques resulted in higher phenol concentrations in cooling towers at an oil refinery, indicating that biooxidation may be a significant removal mechanism. These studies indicate the feasibility of removing organic water contaminants in cooling towers; organic loadings were not stated but were presumably relatively low. However, no information concerning volatile organic emissions from the towers was collected so that the fraction of organic removal due to physical stripping, compared to that removed by bio-oxidation, could not be determined.

### 1.2 Chemical Oxidation

Sadana and Katzer (1974) conducted atmospheric pressure experiments to determine the rate of catalytic chemical oxidation of phenol. At 100° C, with very high catalyst loadings (46.5 g/L Harshaw Cu 0803), the half life of phenol at an initial concentration of 11 g/L was nearly two days. In a test conducted with 3.68 g/L catalyst a half life of approximately 85 hours was determined for a solution of 102 g/L of phenol. The focus of these experiments was catalysis, but a baseline run without catalyst showed "insignificant oxidation over the time period of a typical run" (which seems to be about 110 hours). The limits of analytical detection are not stated, but the data reported suggest that a 1% decrease in phenol would be detectable.

The experiments were conducted at 100°C whereas cooling towers operate in the range of 30-40°C. Although the solubility of the oxygen is depressed at higher temperatures, the reaction medium was sparged with oxygen in contrast to air which is present in cooling towers. The five fold increase in partial pressure would more than compensate for the increased Henry's law constant (i.e., from $5.5 \times 10^{-4}$ atm/mole fraction to $7.0 \times 10^{-4}$ atm/mole fraction). Chemical oxidation of phenol appears to be an insignificant removal mechanism under cooling tower conditions.

### 1.3 Vapor Phase Emissions

Cooling towers in the coke by-product recovery industry are used to cool direct-contact water that has been contaminated with organics from the process stream. Some organics, primarily naphthalene, are removed from the water by either physical separation of solid naphthalene or by passing water through a tar-bottoms reservoir to dissolve the naphthalene and other organics. An initial environmental assessment study of coke oven by-product plants by Van Osdell, et al (1979) found a benzene concentration of 15.8 mg/m$^3$ above a cooling tower; in addition, other organic compounds were identified. Emission tests were conducted at three other by-product plants by the EPA Emissions Measurement Branch (1981 a, b, c) and yielded emission factors of 270 g benzene/Mg coke for direct-water cooling towers and 70 g benzene/Mg coke for tar-bottom cooling towers. Emission rates varied from 5.5 Kg/hr for the tar bottom to 33 Kg/hr for the direct water. Other relevant test data are summarized in Table 1.

These data from industrial cooling towers in coke by-product recovery plants demonstrate that environmentally significant organic emissions can be produced by cooling towers using water containing only a few mg/L contaminant. One of the objectives of the present investigation was to determine the type and extent of wastewater pretreatment necessary to eliminate or reduce to acceptable levels any atmospheric releases of organic material from cooling towers receiving make up water contaminated with organic chemicals. Solvent extraction, followed by ammonia stripping, of contaminated water from coal gasification plants was expected to reduce the potential cooling tower emissions from towers utilizing such wastewater as makeup to an acceptable limit.

TABLE 1. BENZENE EMISSIONS FROM COOLING TOWERS
(U.S. EPA, 1981 a, b, c)

| Location | CF&I Pueblo, CO | U.S. Steel Fairless Hill, PA. | Bethlehem Steel Bethlehem, PA |
|---|---|---|---|
| Benzene emissions Kg/hr | 5.41 | 31.9 | 33.4 |
| Stack velocity, m/min | 435-543 | 370-520 | 262-276 |
| Air flow, Nm$^3$/min | 10900-13300 | 7220-10400 | 12200-12900 |
| Cold well, mg/L benzene | 7.5 | 1.0 | 3.5 |
| Hot well, mg/L benzene | 68 | 48 | 6.8 |
| Type of cooling tower | tar bottom | direct water | direct water |
| Stack area, m$^2$ | 29.2 | 21.1 | 49.4 |

Mohr and King (1984) have identified dimethylhydantoin and related polar compounds in coal gasification condensate water from the University of North Dakota Energy Research Center slagging gasifier. A significant fraction of the chemical oxygen demand (COD) in many condensate waters is composed of compounds which are more polar than phenol. These polar compounds are not effectivey removed by extraction with common solvents such as diisopropyl ether or methyl isobutyl ketone. In addition, these polar compounds are not extracted by methylene chloride so they are not successfully quantitated by the GC/MS analytical techniques which are conventionally used to study these condensate streams. High performance liquid chromatography was used to identify the hydantoins in the wastewater sample.

## 1.4 Drift Emissions

In addition to atmospheric emissions from organics being evaporated into the cooling tower exhaust, water droplets are ejected from the cooling tower as "drift". Vertical air velocity through cooling towers typically varies from 90 to 200 m/min (Burger, 1975). A baffle or drift elimination system is placed between the water distribution system and the air discharge point to minimize the dispersal of entrained water droplets. Drift minimization is essential for the conservation of water, the retention of chemical treatment additives in the cooling tower and the prevention of damage by the chemical additives to vegetation in the surrounding area. A common method of trying to improve cooling tower performance is to increase the air velocity by increasing the fan power and pitch angle. This often causes increased drift loss. An acceptable level of drift generally considered satisfactory, is "not in excess of 0.2 percent" of the water circulation rate (Burger, 1975). Much lower drift levels can be achieved.

## 1.5 Biological Emissions

Another environmental aspect of cooling tower operations, emissions of pathogenic bacteria, involves somewhat different considerations than stripping or chemical and biological oxidation. While the oxidative processes may be insignificant in reducing liquid phase concentrations (compared to stripping), they may be highly significant in the production of pathogenic organisms or partially oxidized materials in the vapor and drift.

## 1.6 Summary

In summary, atmospheric emissions from cooling towers are potentially significant. In one investigation, involving the treatment of selected aqueous kraft mill wastes in a cooling tower (Georgia Kraft Co., 1971), organics were removed predominantly by air stripping, with biological activity playing only a very minor role. The results of this study may have been somewhat compromised in that there was no pretreatment to remove reduced sulfur compounds, which are known to inhibit certain types of biodegradation. Nevertheless, the results point to a significant potential for atmospheric emissions of wastewater contaminants since 25 to 30 percent of the BOD reduction was attributed to physical stripping of volatile components.

Normally, cooling towers are regarded as devices in which a single process is occurring-simple evaporative cooling of a liquid stream. However, the presence of mineral contaminants introduces potential environmental problems associated with the release of these contaminants to the neighboring air. Typical problems include crop damage and corrosion of machinery as a result of salt deposition. Further introduction of organic contaminants--as in synfuels condensates--greatly complicates the possible emissions. A number of the ingredients of synfuels condensates--notably phenols, ammonia, and sulfur compounds--are not only toxic but volatile as well. One would expect these materials to be stripped from the wastewater very rapidly in normal cooling tower operation. Entrainment, chemical oxidation, and biological oxidation can also be expected to occur within the cooling tower with environmental emissions as indicated:

Stripping -- Vapor phase contaminant emission
Entrainment -- Aerosol contaminant emission
Chemical Oxidation -- Vapor and aerosol emissions of oxidized material
Biological Oxidation -- Vapor and aerosol emissions of oxidized material, metabolites, and possibly pathogenic bacteria

Available information, as well as conventional wisdom, suggest that stripping and aerosol formation are the dominant mechanisms of concern; chemical oxidation and biological treatment are probably much less important in the cooling tower environment.

## 2.0 SUMMARY AND CONCLUSIONS

A computer program was developed which calculates the atmospheric emissions of contaminants in the makeup wastewater as a function of cooling tower operating conditions. The stripping of volatile components is estimated using Antoine-type (Smith and Van Ness, 1975) apparent vapor pressure data. Biological oxidation is incorporated in the model as a removal mechanism for organics based on suspended growth kinetics developed for coal gasification wastewater treatment. These kinetic data have been adapted to apply to fixed film oxidation by organisms growing on the surface of the tower packing.

A study of potential emissions from counterflow cooling towers operated with partially treated wastewater from coal gasification plants was conducted to estimate the magnitude of these emissions and to determine the effect of cooling tower operating conditions on these emissions. Two separate laboratory scale cooling systems were operated. A 5 cm (2 in) diameter packed column was built and operated first, and variables such as liquid-to-gas ratio, inlet liquid temperature, cycles of concentration and makeup composition were investigated. The relatively low gas throughput of this column made it feasible to substitute nitrogen for air during selected tests. The 5 cm diameter column was operated primarily with a synthetic wastewater which had a composition similar to that of the University of North Dakota Energy Research Center's slagging gasifier process wastewater which had been subjected to solvent extraction and steam stripping yet still contained substantial quantities of dissolved organic and inorganic contaminants. The column was also tested with actual pretreated gasification wastewater which was produced in the University of North Dakota Energy Research Center (UNDERC) slagging gasifier and then solvent extracted and steam stripped at UNDERC. The bulk of the cooling tower tests were conducted under conditions which would inhibit biological oxidation of organics.

After the 5 cm diameter cooling tower had been tested, a 30 cm (12 in) square by 91 cm (36 in) high cooling tower, representing a scaleup factor of approximately 46, was operated. The testing program for the larger cooling tower tests was designed to establish the influence of cycles of concentration and liquid-to-gas ratio on cooling tower emissions under conditions which would inhibit biological oxidation of organics and under conditions (packing type/area, liquid/gas velocities) more representative of commercial towers.

The composition of the cooling tower makeup in the larger cooling tower was the same as that used in the earlier experiments in the 5 cm diameter cooling tower. In one test, however, cooling tower additives (anti-foam, sodium metaphosphate and potassium dichromate) were also present. One test was conducted after a period of continuous operation to promote the growth of biomass on the tower packing and walls to determine the effect of biological oxidation on removal of organic species in the circulating water.

The results of the laboratory experiments indicated that cooling tower operating parameters such as liquid-to-gas ratio and inlet water temperature have little influence on atmospheric emissions of contaminants at a given cycles of concentration. This is consistent with the mathematical model which links the evaporation of water to the stripping of contaminants by the ratio of the apparent vapor pressure of the contaminant to the vapor pressure of water. While both of these quantities change with temperature, the ratio of the two quantities is nearly constant over the range of cooling tower temperatures for several of the contaminants investigated in this study. The cycles-of-concentration, (i.e., the ratio of the makeup flowrate to the blowdown flowrate, assuming insignificant drift loss) is the primary influence on the amount of volatile contaminants in the blowdown. By fixing the fraction of the makeup water which is to be evaporated, the fraction of the contaminants in the makeup which will be evaporated is also fixed. The capacity of the tower for transfer of water between the liquid and gas phases is an input to the mathematical model which characterizes the cooling tower. This capacity is also used to describe the transfer of contaminants between phases.

Operation of the 5 cm diameter laboratory cooling tower with nitrogen instead of air did not produce a significant change in the mass of phenol, methanol, and acetone recovered in the cooling tower blowdown. With both chemical and biological oxidation mechanisms eliminated, the composition of the circulating coolant did not change at a given cycles of concentration, thus implying that these mechanisms are of minor importance. This was observed both when actual and when synthetic pretreated wastewater was used as makeup. Similarly, operation under conditions designed to promote bioactivity did not produce a significant change in the recovery of volatile organics in the tower blowdown. However, the mathematical model predicts that a substantial amount of phenol could be removed through biological oxidation. This mechanism would not have a major effect on the amount of phenol recovered in the blowdown.

Phenol removed by biological oxidation would decrease the driving force for stripping of phenol and thus decrease air emissions. The more volatile components (methanol, acetone, and acetonitrile) are almost entirely removed by stripping and this is to be expected in the presence or in the absence of bioactivity.

Based on concentrations of contaminants in the tower blowdown, no significant differences were observed in scaling up from the 5 cm diameter tower to the 30 cm square tower. Model predictions of the role of bioactivity on organic contaminant removal are very sensitive to the specific surface area of tower packing material. Thus, predictions of the potential role of biological oxidation in contaminant removal are much higher for the 5 cm diameter column than for the 30 cm square column because the packing used in the 5 cm diameter column had a much greater specific surface area than the packing used in the 30 cm square column. Application of the cooling tower model to a much larger experimental system with lower surface area predicts a reduced but measurable degree of biological oxidation of phenol. More volatile components are predicted to be almost completely stripped (i.e., not biologically oxidized) under actual cooling tower operating conditions.

In Summary:

- A mathematical model describing mass and heat transfer and biological oxidation in counterflow cooling towers was developed.
- Two laboratory counterflow cooling systems were built and operated.
- Air stripping data obtained from these systems was consistent with model predictions.
- The relatively minor effect of biological oxidation on contaminant levels, predicted by the model made it impossible to completely verify the accuracy of the model in describing this mechanism.

# 3.0 MATHEMATICAL MODELING OF EMISSIONS FROM COOLING TOWERS

## 3.1 Description

A mathematical model has been developed to predict the fate of contaminants present in counterflow cooling tower makeup. The inputs to the program describe the inlet liquid and inlet air streams and the tower characteristics. Based on these data an iterative procedure is used to calculate temperature and liquid and gas flowrates as a function of position in the tower. With this established, stripping calculations are made based on pollutant characteristics (makeup concentration, Antoine-type [Smith and Van Ness, 1975] vapor pressure data) using the same mass transfer characteristics as were used for the air/water system. Simultaneously, biological oxidation calculations are made based on kinetic data for coal gasification wastewater reported in Hicks, et al (1979), with adjustments for temperature changes. A generalized flow sheet for the model is given in Figure 1. The Fortran source code is given in Appendix A. The program, as written, was run on a Digital Equipment Company VAX computer. With slight modifications, it has also been run on an IBM personal computer. These modifications are described in Appendix A.

Equations 1 through 8 describe the humidification of air in the cooling tower (see nomenclature list given in Table 2 at the end of this section). The development of these equations from differential mass and energy balances is given in Treybal, 1968. Equations (2) and (5) are statistical fits of the psychrometric data for air and water at one atmosphere (Treybal, 1968).

$$G'\frac{dH'}{dt} = K_y a\,(H_i'-H) \qquad (1)$$

$$H_i' = 0.24\,(t_L-32) + Y_i\,0.5\,(t_L-32) + Y_i\,(1075) \qquad (2)$$

$$G'\frac{dY}{dz} = K_y a\,(Y_i-Y) \qquad (3)$$

$$Y_i = 18\,\frac{P_{H_2O}}{P_T} \Big/ 29\left(1-\frac{P_{H_2O}}{P_T}\right) \qquad (4)$$

$$\ln P_{H_2O} = (16.806-9442.23/(t_L+460)) \qquad (5)$$

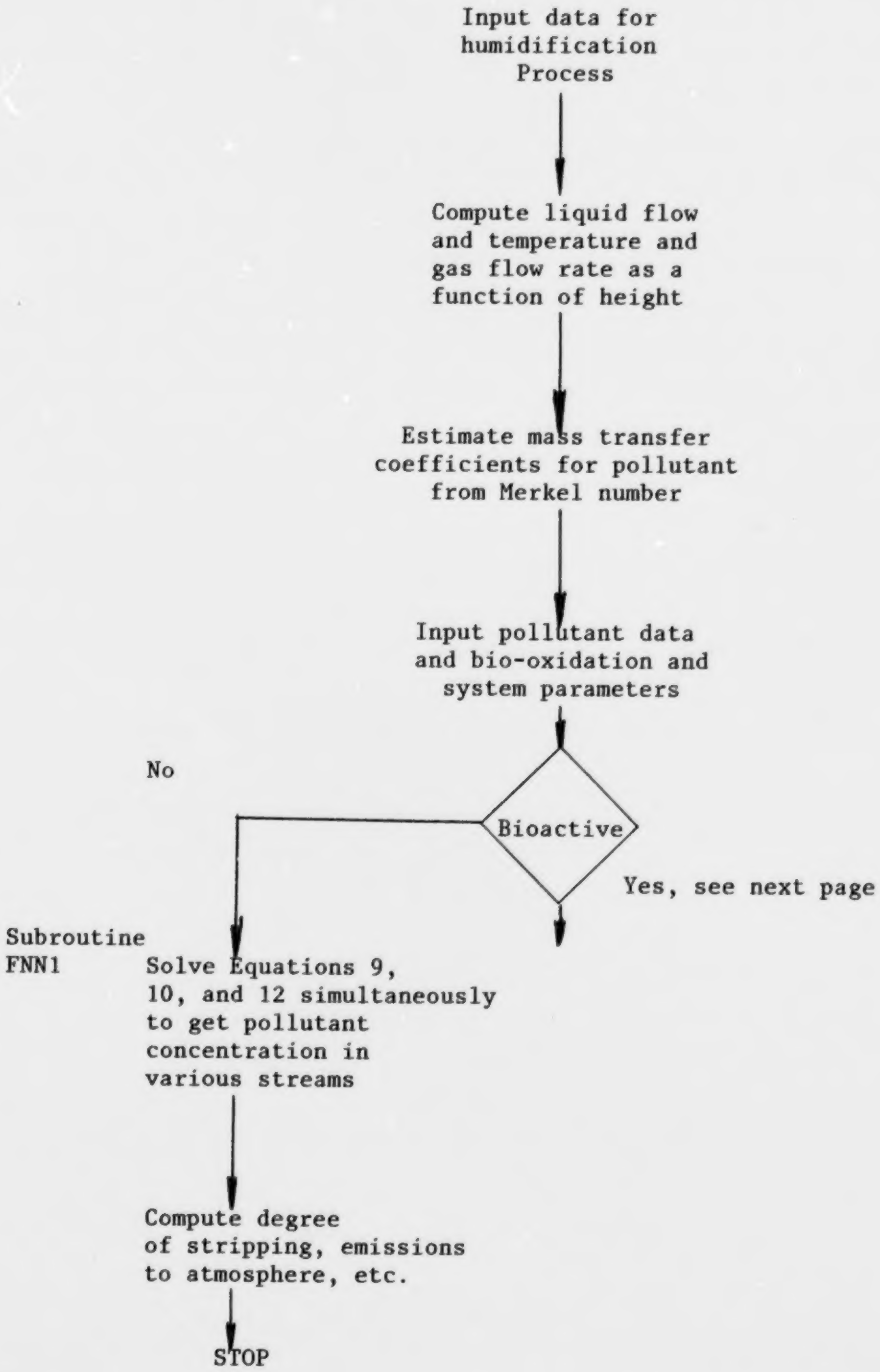

Input data for humidification Process
Compute liquid flow and temperature and gas flow rate as a function of height
Estimate mass transfer coefficients for pollutant from Merkel number
Input pollutant data and bio-oxidation and system parameters
No
Bioactive
Yes, see next page
Subroutine FNN1
Solve Equations 9, 10, and 12 simultaneously to get pollutant concentration in various streams
Compute degree of stripping, emissions to atmosphere, etc.
STOP

Figure 1. Mathematical Model Flowsheet

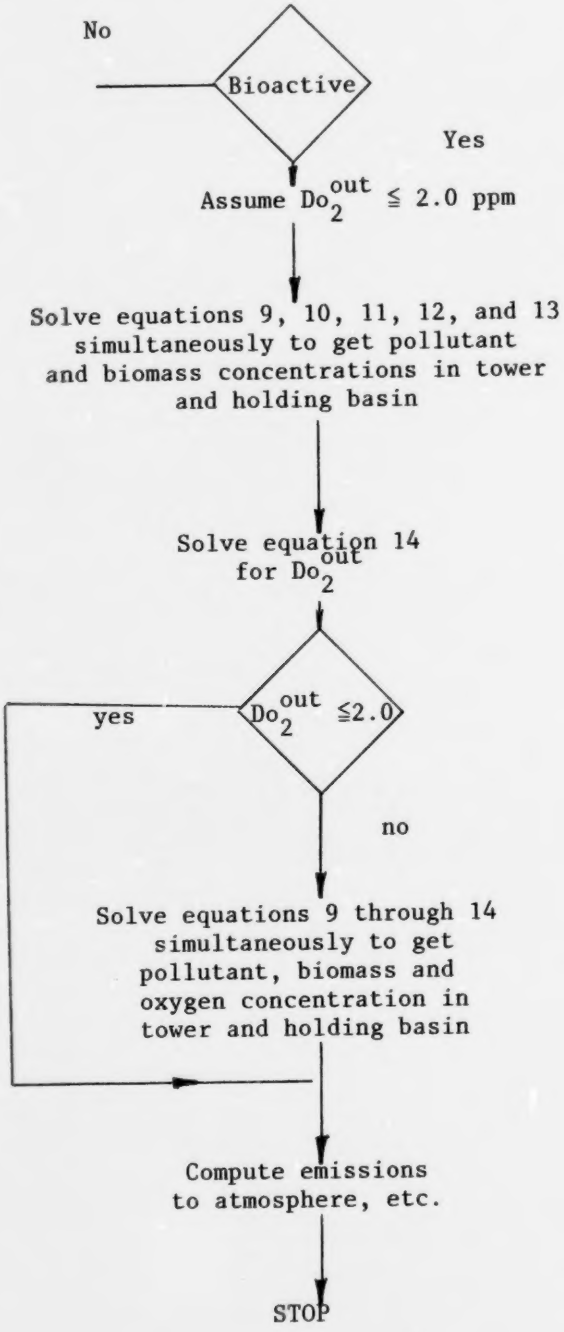

No
Bioactive
Yes
Assume $Do_2^{out} \leqq 2.0$ ppm
Solve equations 9, 10, 11, 12, and 13 simultaneously to get pollutant and biomass concentrations in tower and holding basin
Solve equation 14 for $Do_2^{out}$
yes
$Do_2^{out} \leqq 2.0$
no
Solve equations 9 through 14 simultaneously to get pollutant, biomass and oxygen concentration in tower and holding basin
Compute emissions to atmosphere, etc.
STOP

Figure 1 (continued). Mathemtical Model Flowsheet

$$\frac{dL'}{dt} = \frac{G'dY}{dz} \qquad (6)$$

$$\frac{dL't_L}{dz} = \frac{G'dH'}{dz} \qquad (7)$$

$$\bar{G}' = G' \,(1/29 + Y/18) \qquad (8)$$

These equations are integrated to give the molar gas flow rate, $\bar{G}'$, liquid flow rate, $L'$, and the bulk liquid temperature, $t_L$, as function of height above the bottom of the packing, Z. Integration is carried out from the bottom to the top of the cooling tower. The liquid flow rate, $L'$, and temperature $t_L$, are specified at the top of the tower so values of $L'$, and $t_L$ are assumed at bottom and integration proceeds. If the calculated values of $L'$ and $t_L$ at the top of the tower are the same as those specified then the integration of the humidification equations is complete. If the calculated values do not agree with the specified values then the Solve subroutine using the method of Broyden computes better estimates of $L'$ and $t_L$ at the bottom of the tower and the integration is repeated.

For an individual contaminant, the removal mechanisms due to stripping and biological oxidation are described by equations 9 and 10. The biomass balance is described by equation 11. These equations incorporate Michaelis-Menton type kinetics. Rate data is available in Hicks, et al (1979) for wastewater from the Synthane process.

$$\frac{dL'Xs}{dz} = 18\, k_y a \left( \frac{HXs}{P_T} - Y_s \right) + C_1 \left( f_1 X_B + aK_t \right) \left( \frac{kX_s f_{xs}}{X_s f_{xs} + K_s} \right) \qquad (9)$$

where $C_1 = \dfrac{28.3\ (18)\ \text{lb mol liter}}{(J)24(32)(1000)(454)\ \text{mg ft}^3\text{hr}}$

and $f_{xs} = 32 \times 10^{-6}$ J mg BOD/18.0 liter

J = stoichiometric ratio = gmol $O_2$ required to oxidize 1 gmol of pollutant

$$\ln H = \ln(\gamma_s P_{svap}) = (A_s + B_s/(t_L+460))$$

$$\frac{d\bar{G}'Y_s}{dz} = k_y a\left(\frac{HX_s}{P_T} - Y_s\right) \qquad (10)$$

$$\frac{dL'X_B}{dz} = -C_2\ (f_1X_B+aK_t)\left(\frac{Y_B k X_s f_{xs}}{k_s+X_s f_{xs}} - k_d\right) \qquad (11)$$

where $C_2 = \frac{62.4 \text{ lb day}}{24 \text{ ft}^3 \text{ hr}}$

These equations are integrated from the bottom of the cooling tower to the top to obtain the inlet and outlet concentrations of biomass in the water, ($X_B$) and pollutant in the water and gas ($X_s$ and $Y_s$). The outlet liquid is the input to the holding basin and inlet liquid to the tower is the output of the holding basin. Thus, the flow rate and composition of the liquid stream in the tower must be consistent with the biomass, pollutant and oxygen balances for the holding basin.

Biological oxidation, but not stripping, also takes place in the holding basin (i.e., the cold well). For an individual pollutant the concentration in the holding basin is described by equation 12.

$$\frac{L_o'AX_{so}}{18} + \frac{MAC_s 10^{-6}}{(MW_s)} - (L_z' + D+B)\ \frac{AX_{sz}}{18} - C_3R_s = 0 \qquad (12)$$

where $C_3 = \frac{28.3 \text{ l day(mol oxygen)lb}}{(24)(32)(454{,}000)\text{J ft}^3\text{hr(g oxygen) mg}}$

$$R_s = \frac{r(V_H)k\ X_{sz}f_{xs}}{K_s + X_{sz}f_{xs}}$$

and $r = 1$ if $Do_2^{out} \geq 2$ mg/L

$r = \frac{Do_2^{out}}{2}$ if $Do_2^{out} < 2$ mg/L

The rate of biological oxidation is independent of oxygen concentration if dissolved oxygen is greater than 2 mg/L. The biomass balance in the holding basin is given by Equation 13.

$$(0.454)L_o'AX_{B_o} + \frac{28.3\ Y\ (R_s)}{24.0} - (L_z'+D+B)AX_{B_z}\ (0.454) - \frac{28.3\ k_d X_{B_z} V_H}{24} = 0 \qquad (13)$$

The oxygen concentration in the holding basin is calculated using equation 14 to determine if this is a limiting factor in biological oxidation.

$$L_o'A\ Do_2^{in}\ 10^{-6} - (L_z'+D+B)\ A\ Do_2^{out} 10^{-6} - \frac{28.3\ (R_s)}{24(1000)(454)} = 0 \qquad (14)$$

where $Do_2^{in}$, in the inlet oxygen concentration to the holding basin is assumed to be the saturated concentration at the temperature of the outlet liquid stream from the cooling tower.

Nomenclature for the above discussion is given in Table 2.

## TABLE 2. NOMENCLATURE FOR EQUATIONS 1-14

| | | |
|---|---|---|
| $G'$ | Dry gas flow rate | $lb/(ft^2hr)$ |
| $H'$ | Enthalpy of the gas | Btu/lb dry air |
| $H'_i$ | Enthalpy of the gas phase at the gas/liquid interface | Btu/lb dry air |
| $K_ya$ | Overall gas phase mass transfer coefficient for water based on humidity as the driving force | lb $H_2O/ft^3$ hr |
| Z | Height above bottom of packing | ft |
| $t_L$ | Liquid temperature | °F |
| Y | Humidity of the bulk gas | lb $H_2O$/lb dry air |
| $Y_i$ | Humidity of the gas at gas/liquid interface | lb $H_2O$/lb dry air |
| $P_{H_2O}$ | Vapor pressure of water | psia |
| $P_T$ | Total pressure | psia |
| $L'$ | Liquid flow rate | $lb/(ft^2\ hr)$ |
| $\bar{G}'$ | Total molar gas flow rate | lb $mol/(ft^2\ hr)$ |
| $X_s$ | Mole fraction of pollutant in liquid | |
| $k_ya$ | Mass transfer coefficient for pollutant based on mole fraction as driving force | lb $mol/(ft^3\ hr)$ |
| H | Product of the pollutant activity coefficient and pollutant vapor pressure | psia |
| $Y_s$ | Mole fraction of pollutant in the bulk gas | |
| $f_1$ | Fractional liquid holdup in the packing | $ft^3$ liquid/$ft^3$ packing |
| $X_B$ | Concentration of biomass | mg/liter |
| a | Specific surface area of the packing | $cm^2$ surface/$cm^3$ packing |
| $K_t$ | Loading of biomass on packing | mg/liter |
| $f_{xs}$ | Factor converting mole fraction of pollutant to mg BOD/liter | mg BOD/liter |

TABLE 2. continued

| | | |
|---|---|---|
| $\gamma_s$ | Activity coefficient for the pollutant | |
| $P_{svap}$ | Vapor pressure of the pollutant | psia |
| $A_s, B_s$ | Antoine parameters for H | |
| $k, K_s, k_d, Y_B$ | Michaelis-Menton parameters | k = gBOD/(g biomass day)<br>$K_s$ = mg BOD/liter<br>$k_d$ = day-1<br>$Y_B$ = mg biomass/mg BOD |
| A | Cross sectional area of cooling tower | $ft^2$ |
| M | Makeup rate | $lb/(ft^2\ hr)$ |
| $C_s$ | Concentration of pollutant in makeup | mg/L |
| $(MW)_s$ | Molecular weight of pollutant | |
| D | Drift rate | $lb/(ft^2\ hr)$ |
| B | Blowdown rate | $lb/(ft^2\ hr)$ |
| $V_H$ | Volume of holding basin | $ft^3$ |
| $Do_2^{in}$ | Dissolved $O_2$ in the inlet stream of the holding basin | mg/L |
| $Do_2^{out}$ | Dissolved $O_2$ in the outlet stream of the holding basin | mg/L |
| Subscripts: | | |
| o | bottom of the cooling tower | |
| z | top of the cooling tower | |

## 3.2 Use of the Model

Input to the program is specified using an eleven line data file which is read from the main program. The data file must be named CT.DAT. Format for CT.DAT is given in Table 3. The definition of the specified inputs are given in Table 4.

The model is structured to permit the calculation of the fate of one contaminant at a time. By substituting vapor pressure and makeup concentration data for different contaminants, predictions for individual contaminants present in the wastewater can be made in a series of model runs. Individual components are dilute relative to the concentration of water so the interaction has been assumed. Similarly, the best biokinetic data available for coal gasification wastewater are used in the model, however, these data can be varied in the event that more precise information is available for the particular wastewater to be considered.

Model runs were made for phenol, methanol, acetone, and acetonitrile. Vapor pressure inputs for phenol were based on data from Hicks, et al (1979) using a procedure described in Section 3.3. Vapor pressure inputs for methanol, acetone, and acetonitrile were based on vapor pressure data from Perry and Chilton (1973) and activity coefficients estimates from Reed, et al (1977). For ionizable species (e.g., ammonia, hydrogen cyanide) stripping predictions can be generated in the same manner as for non-ionizable species if vapor pressure data accurate at the pH of the circulating coolant are used as input to the model.

The efficiency of a cooling tower for evaporation of water is represented by the "tower characteristic" or the Merkel number of the tower. In the formulation of the model this Merkel number is also used to calculate the efficiency of the tower for stripping. This number

$$(K_y a)Z/L' = \int_{T_2}^{T_1} dT/(h'-h) \qquad (15)$$

where $T_1$ = inlet water temperature °F
$T_2$ = outlet water temperature °F
$h$ = enthalpy of air Btu/lb dry air
$h'$ = enthalpy of saturated air at water temperature Btu/lb dry air

is generally used for packing selection in the design of cooling towers. For

TABLE 3. FORMAT FOR CT.DAT

---

NBS

PT,ZM,Z,CAREA

FL,SAREA,PDRIF

VH,CC

GP,XHO,YO

TLZ,ZLZ

X1(1), X1(2), ER1, IT1, D

AS, BS, STOICH, CS, SMW

AKO, AKS, AKD, Y, AKT, TREF

X2(1), X2(2), X2(3)

ER2, IT2, D

## TABLE 4. INPUT DATA FOR CT.DAT

---

NBS = 0 if sterile, 1 if bioactive

PT = Total pressure, psia

ZM = Merkel number

Z = Tower height, ft

CAREA = Cross sectional area of tower, $ft^2$

FL = Liquid hold up $ft^3$ liq/$ft^3$ tower

SAREA = Specific area of packing $ft^2$ surface/$ft^3$ tower

PDRIF = Percent of recirculation that becomes drift

VH = Volume of holding basin, $ft^3$

CC = Cycles of concentration

GP = Gas flow rate, lb dry air/($ft^2$ hr)

XHO = Enthalpy of inlet air, Btu/lb dry air

YO = Humidity, lb $H_2O$/lb dry air

TLZ = inlet temperature of liquid to tower, °F

ZLZ = Liquid circulation rate, lb/($ft^2$ hr)

X1(1) = Initial estimates of outlet liquid flow rate from tower, lb/($ft^2$ hr) (ZLZ is generally close enough)

X1(2) = Initial estimate of outlet liquid temperature, °F

ER1 = Convergence parameter, use 0.0001

IT1 = Number of iterations, use 50

D = Option parameter, use -1.0

$\left.\begin{array}{l}\text{AS}\\ \text{BS}\end{array}\right\}$ specify such that $\gamma_s P_s = EXP(AS + BS/T)$

where $P_s$ = vapor pressure of pollutant, psia

$\gamma_s$ = activity coefficient

and T = temperature °R = °F +460

TABLE 4. (continued)

STOICH = lb mol $O_2$ needed for biooxidation per lb mole of pollutant

CS = concentration of pollutant in makeup, mg/L

SMW = molecular weight of pollutant

AKO = Michaelis-Menton parameter; g BOD/(g biomass)(day)

AKS = Michaelis-Menton parameter; mg BOD/liter

AKD = Michaelis-Menton parameter; $day^{-1}$

Y = Michaelis-Menton parameter; mg biomass/mg BOD

AKT = Monolayer packing constant = 1.333E-4 g

TREF = Reference temperature for Michaelis-Menton parameters, °F X2(1)

= Initial estimate of pollutant concentration in liquid outlet stream of tower, mole fraction

X2(2) = initial estimate of biomass concentration in liquid outlet stream of tower, mg/liter

X2(3) = initial estimate of $O_2$ concentration in liquid outlet stream of holding basin, mg/L

ER(2) = convergence parameter, use 0.00001

IT2 = convergence parameter, use 50

D = convergence parameter, use -1.0

determination of the actual tower characteristics under operating conditions, a numerical integration technique is employed (Perry and Chilton, 1973) where

$$(K_y a)Z/L' \approx \frac{T_1-T_2}{4}\left(\frac{1}{\Delta h_1} + \frac{1}{\Delta h_2} + \frac{1}{\Delta h_3} + \frac{1}{\Delta h_4}\right) \qquad (16)$$

where $\Delta h_1$ = $(h_w-h_a)$ at $T_2 + 0.1\ (T_1-T_2$
$\Delta h_2$ = $(h_w-h_a)$ at $T_2 + 0.4\ (T_1-T_2)$
$\Delta h_3$ = $(h_w-h_a)$ at $T_1 - 0.4\ (T_1-T_2)$
$\Delta h_4$ = $(h_w-h_a)$ at $T_1 - 0.1\ (T_1-T_2)$

and

$h_w$ = enthalpy of wet air at water temperature, Btu/lb dry air
$h_a$ = enthalpy of wet air at wet bulb temperature, Btu/lb dry air

A table of enthalpy data is given in Appendix B. This table, along with $T_1$, $T_2$, the wet bulb temperature of the entering air and the liquid to gas ratio can be used to calculate tower characteristics (Merkel numbers) for operating cooling towers.

### 3.3 Vapor Pressure Data for Use in the Mathematical Model

Stripping calcuations are based on vapor pressure data supplied for individual wastewater components. The vapor pressure data are input to the program as coefficients in an Antoine-type equation,

$$\ln(\Upsilon_s P_s) = A_s + B_s/(t+460) \qquad (17)$$

where $\Upsilon_s$ = activity coefficient
$P_s$ = pure component vapor pressure, psia
$A_s$ and $B_s$ are constants
and t = temperature, °F

For purposes of model testing, runs were made to predict the fate of phenol, methanol, acetone, and acetonitrile. Pure component vapor pressure were obtained from Perry and Chilton (1973). Activity coefficients for methanol, acetone and acetonitrile were obtained from Reed et al (1977). Because of the importance of phenol in coal gasification wastewater streams, and because accurate azeotropic composition data were available for this compound, a more elaborate procedure was employed to calculate the inputs to the model for phenol. Vapor pressure data are given in Table 5. In addition, the relative volatility as defined by

$$\alpha = \frac{\gamma_s P_s}{P_{H2O}} \tag{18}$$

are given for acetonitrile, acetone, methanol, and phenol.

The vapor pressure data for phenol were calculated from vapor liquid equilibrium data presented in Hicks, et al (1979). Since these data are based on actual observation, they are expected to lead to better vapor pressure estimates than those based on correlation of activity coefficients. To mathematically describe the observed deviation of the phenol-water mixture from ideal solution behavior, it is necessary to select an appropriate activity coefficient model. Hicks, et al (1979) used the binary form of the van Laar equation (Smith and Van Ness, 1975), to correlate experimental phenol-water phase equilibrium data at several different combinations of system temperature and pressure. It was determined that the simple two-parameter model was adequate to represent the equilibrium behavior. Another advantage for the van Laar form, according to Smith and van Ness (1975), is that the two fitting parameters may be assumed to be independent of pressure at low to moderate pressures, such as 1 atm. Therefore, because of its proven usefulness and simplicity, the van Laar model was used in this investigation.

The van Laar activity coefficient model relates the liquid-phase phenol concentration to the activity coefficient as follows:

$$\ln \gamma_p = \frac{A_m}{\left(1 + \frac{A_m}{B_m}\frac{X_p}{X_w}\right)^2} \tag{19}$$

where $A_m$ and $B_m$ are the temperature-dependent van Laar parameters, and $X_p$ and $X_w$ denote the aqueous mole fractions of phenol and water, respectively. The phenol concentration in the cooling tower is low enough ($X_p/X_w < .00006$) that Equation 19 may be simplified to its limiting "infinite dilution" form:

$$\ln \gamma_p^{\infty} = A_m \quad (\text{as } X_p \rightarrow 0) \tag{20}$$

TABLE 5. VAPOR PRESSURE AND RELATIVE VOLATILITY DATA FOR MODEL VERIFICATION

|  | T(°F) | $\gamma_s P_s$ (psia) | Relative volatility | $A_s$ | $B_s$ |
|---|---|---|---|---|---|
| Acetonitrile | 80 | 10.52 | 20.75 |  |  |
|  | 120 | 16.04 | 9.476 | 8.477 | -3307.0 |
| Acetone | 80 | 18.65 | 36.78 |  |  |
|  | 120 | 63.43 | 37.46 | 16.211 | -7209.7 |
| Methanol | 80 | 4.346 | 8.572 |  |  |
|  | 120 | 11.98 | 7.078 | 11.690 | 5552.6 |
| Phenol | 80 | 0.739 | 1.458 |  |  |
|  | 120 | 2.629 | 1.553 | 18.084 | -9916.9 |
| Water | 80 | .507 | 1.0 |  |  |
|  | 120 | 1.693 | 1.0 |  |  |

Note: 1 atm = 14.7 psia

Values of $A_m$ at various temperatures were calculated from the vapor-liquid equilibrium data of Hicks et al (1979), who presented a plot of $Y_p$ versus $X_p$ at several different total pressures. The isobaric equilibrium lines shown on Hicks' plot were generated from the van Laar activity coefficient model after it had been correlated to the experimental data. For a two-component, two-phase system, the Gibbs phase rule states that the temperature is uniquely defined at a fixed pressure (one atmosphere in this case) and a fixed liquid-phase composition. In this study, the simplifying assumption will be made that the temperature of the liquid mixture at a given system pressure is essentially the boiling point of water at that pressure.

The procedure for determining the van Laar parameter $A_m$ as a function of temperature is straightforward. The temperature and pressure dependency of the activity coefficient is given by the differential equation for a constant-composition solution.

$$d(\ln \Gamma_i) = d\left(\frac{\bar{G}_i^E}{RT}\right) = \frac{-\overline{\Delta H}_i}{RT^2}\, dT + \frac{\overline{\Delta V}_i}{RT}\, dP, \qquad (21)$$

where $\bar{G}_i^E$ = partial molal excess Gibbs free energy

$\overline{\Delta H}_i$ = partial molal heat of mixing

$\overline{\Delta V}_i$ = partial molal volume change of mixing.

and $T$ = temperature, °K.

In the dilute concentration region of interest in this development, the volume change of mixing will approach a value of zero in the limit as the phenol concentration becomes very small. Thus, is the extreme case of infinite dilution the quantity $\overline{\Delta V}_i^{\infty}$ is identically zero, thereby eliminating the pressure dependency term in Equation (21). Integration of the remainder of Equation (21), assuming a constant partial molal heat of mixing, gives rise to the following equation:

$$\ln\gamma_i^\infty = \frac{\overline{\Delta H}_i^\infty}{R}\,\frac{1}{T} + b_m \qquad (22)$$

Replacing the quantity $(\overline{\Delta H}_i^\infty/R)$ by the constant $a_m$, the two constants $a_m$ and $b_m$ can be used for statistical fitting purposes. Now, by combining Equations (20) and (22) for infinite dilution of phenol in water, the temperature dependency of $\gamma_p^\infty$ and the van Laar parameter A can be expressed as

$$\ln\gamma_p^\infty = A_m = b_m + \frac{a_m}{T} \qquad (23)$$

This equation is linear with respect to the reciprocal temperature, so a simple linear regression of A versus (1/T) from experimental data could be used to determine $a_m$ and $b_m$.

The data of Hicks et al (1979) are ideal for such a correlation effort. Referring to Equation (19), it is apparent that at least two values of the activity coefficient (at two different liquid-phase concentrations) are necessary to determine a value for $A_m$ at a specified temperature. The calculation of $A_m$ was performed at three different total pressures (2.46, 14.7, and 59.8 psia) using phenol mole fractions of 0.01 and 0.02 at each selected pressure. These small mole fractions were used to insure that the calculated van Laar parameter, $A_m$, reflects the equilibrium behavior in the dilute region and to allow the approximation of the solution temperature with the boiling point of pure water at the prevailing pressure. The required activity coefficient data at a given pressure were calculated using Hicks' equilibrium plot to obtain $Y_p$ data at $X_p$ values of 0.0 and 0.02,

$$P_T Y_p = X_p \gamma_p P_p \qquad (24)$$

where $P_p$ = pure component vapor pressure of phenol, psia

Table 6 summarizes the results of the activity coefficient calculations.

Using the resulting data points, two equations in terms of the van Laar parameters $A_m$ and $B_m$ are obtained at each pressure by substitution into Equation (19). Since each system pressure has associated with it a unique temperature, the simultaneous solution of each equation pair results in three values of $A_m$ associated with three different temperatures. The values of the van Laar parameter together with their associated temperatures are given in Table 7. In addition, Table 7 shows the values for A calculated from Equation (23), which was fit to the A versus T data. The correlating equation for the activity coefficient (and the van Laar parameter) was determined using a least squares fit of the data in Table 7 and it has the following form:

$$\ln\gamma_p = 0.508 + \frac{1174.7}{T} \qquad (25)$$

TABLE 6. ACTIVITY COEFFICIENTS FOR PHENOL AS A FUNCTION OF TEMPERATURE AND LIQUID PHASE COMPOSITION

| $P_T$, psia | Temp. °K | Vapor Press Phenol, psia | $X_p = 0.01$ | | $X_p = 0.02$ | |
|---|---|---|---|---|---|---|
| | | | $Y_p$ | $\gamma_p$ | $Y_p$ | $\gamma_p$ |
| 2.46 | 329.7 | 0.0674 | 0.01025 | 37.42 | 0.01425 | 26.01 |
| 14.7 | 373.0 | 0.7090 | 0.0135 | 27.99 | 0.01925 | 19.95 |
| 59.8 | 417.4 | 4.7700 | 0.01475 | 18.46 | 0.02150 | 13.45 |

A comparison of the experimental and calculated values in Table 7 reveals that the correlation method is adequate.

Based on equation (25), the Antoine type vapor pressure data and relative volatilities for phenol were calculated for use in the model. These data are given in Table 5. A similar procedure could be used to obtain more accurate vapor pressure data for methanol, acetone, and acetonitrile if sufficiently accurate vapor liquid equilibrium data were available.

TABLE 7. VAN LAAR'S CONSTANT ($A_m$) FOR PHENOL AS A FUNCTION OF TEMPERATURE

| T, °K | $A_m$ | $A_{cal}$* |
|---|---|---|
| 329.7 | 4.041 | 4.071 |
| 373.0 | 3.723 | 3.657 |
| 417.4 | 3.286 | 3.321 |

*$A_{cal}$ calculated using Equation 23.

# 4.0 EXPERIMENTAL VALIDATION OF THE MATHEMATICAL MODEL USING A SMALL SIMULATOR TOWER

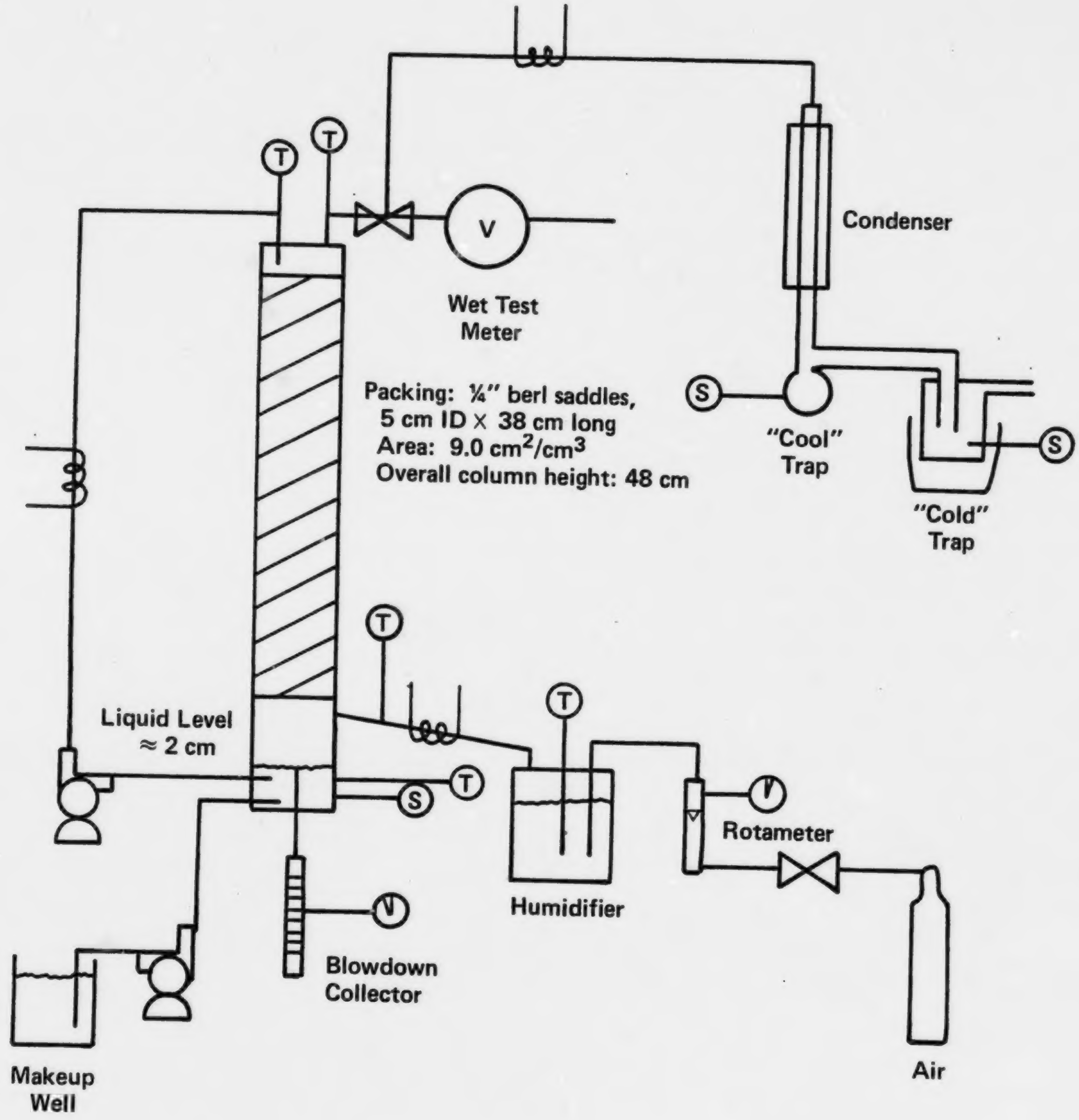
## 4.1 Equipment and Procedure

A small laboratory cooling tower was built and operated to determine potential emissions from cooling towers operated with extracted and stripped coal gasification wastewater. The system was designed to be controllable, and capable of operation over a wide variety of experimental conditions. The small size permitted the enthalpy of the inlet air to be precisely controlled independently of ambient temperature, and since gas flows were relatively low, it was feasible to substitute nitrogen for air in specific tests to determine the extent of biological and chemical oxidation.

The experimental counterflow cooling tower used in this study measured 5 cm in internal diameter and was packed with 38 cm of 0.64 cm (¼ inch nominal) berl saddles. The amount of packing was chosen so that the packed column could accurately simulate an efficient cooling tower as determined by Merkel number. A flow diagram for the experimental system is shown in Figure 2.

Air (breathing grade, USP) was supplied from a high pressure cylinder, passed through a rotameter for flow measurement, saturated by a humidifier at a specific temperature and heated to a controlled temperature before entering the column. Air flow rate was also measured by passing the air leaving the column through a wet test meter. Water was circulated from a sump below the packing to a distributor above the packing using a Milton Roy Model MAI-34-95 packed plunger adjustable stroke metering pump. Water flowrate was determined from a calibration curve prepared for the pump.

A heat load was imposed using a strip heater wrapped around the tube through which the water was circulated. Makeup was added to the cooling tower sump using a Laboratory Data Control Mini Pump with a flow range of 16-160 ml/hr, at a rate sufficient to produce the desired flow of blowdown through an overflow tube in the sump. Blowdown was collected in a graduated cylinder which simplified calculation of this flowrate. Makeup flowrate was adjusted as needed to achieve the desired cycles of concentration.


Condenser
Wet Test Meter
V
T
T
Packing: ¼" berl saddles, 5 cm ID × 38 cm long
Area: 9.0 cm²/cm³
Overall column height: 48 cm
S
"Cool" Trap
"Cold" Trap
S
T
T
Liquid Level ≈ 2 cm
S
T
V
Rotameter
Humidifier
V
Blowdown Collector
Makeup Well
Air

S = Sample Point
T = Temperature Measurement
V = Volumetric Measurement

Figure 2. Small laboratory cooling tower system.

Composite liquid samples (over a discrete time interval) were obtained from the blowdown stream and instantaneous liquid samples were obtained from the sump. The sump was fitted with a septum through which samples could be withdrawn with hypodermic syringes. In addition, air leaving the column was sampled by passing a portion of the air stream through a chilled water condensor and a liquid nitrogen trap. Temperatures were measured at various points in the system as indicated on Figure 2, using Type J thermocouples and a digital thermometer/controller (Omega 4001-JC) which displayed temperatures to the nearest 1°C. The device was also used to control the temperature of the inlet water at the top of the column.

A makeup water of known composition simulating an extracted, stripped gasification wastewater was used for most of the tests in the 5 cm diameter column. The synthetic wastewater was not designed to duplicate that of any particular process, but contained components from a number of chemical groups found in wastewater from various gasification processes including high temperature-entrained flow gasification. The composition is given in Table 8. Hydantoin is a nitrogen heterocyclic compound which is the parent compound of a number of derivatives which have been found in the wastewater from the University of North Dakota Energy Technology Center (UNDERC) gasifier (Mohr, et al, 1983). It has been included at a relatively high level because it is difficult to remove from the raw wastewater by solvent extraction which is a common means of treating this type of stream. Phenol has been included to represent the large number of "phenolic" compounds present in the gasification wastewater, of which phenol itself is generally present at the highest levels. The other organics; methanol, acetone, and acetonitrile are included to represent various groups of compounds which have been found in gasification wastewater. The inorganics; ammonia, cyanide, and thiocyanate are the major inorganic contaminants which have been found in gasification wastewater. Cyanide and thiocyanate were added as sodium salts, ammonia was added as carbonate, bicarbonate, and acetate in different tests.

The makeup water composition given in Table 8 is arbitrary from the standpoint that wastewater produced from different gasification processes can vary widely in composition. In addition, the extent of pretreatment given to a particular raw wastewater prior to use as cooling tower makeup is a variable which may be influenced by cooling tower and cooling system design decisions as well as environmental considerations. The makeup water composition used in this study was strongly influenced by preliminary laboratory studies at RTI which involved preparation of a simulated raw wastewater of the type produced at UNDERC, followed by extraction of the wastewater with di-isopropylether in a separatory funnel extraction scheme simulating six ideal stages. The extracted wastewater was then boiled to simulate a steam stripping process for ammonia removal (without pH adjustment) until the ammonia level was reduced to 280 mg/L. On the basis of subsequent organic analysis of the stripped extracted wastewater it was found that o-cresol, 2,4-dimethylphenol and naphthalene were present in the extracted,

TABLE 8. COMPOSITION OF SIMULATED EXTRACTED AND STRIPPED GASIFIER CONDENSATE

| Component | Concentration mg/L |
|---|---|
| Hydantoin | 2500 |
| Ammonia | 277 |
| Methanol | 238 |
| $SCN^-$ | 210 |
| Phenol | 160* |
| $CN^-$ | 40 |
| Acetone | 10 |
| Acetonitrile | 2 |

*Concentration was doubled for tests 7 and 8.

stripped synthetic wastewater mixture at levels below the reliable detection limit of the gas chromatographic techniques used. These compounds were not included in the makeup water formulation. The formulation which was used in this study may vary considerably from actual makeup water which may be used in large scale plants.

At the beginning of each test, the cooling tower system was loaded with fresh makeup water. The liquid and gas flows were then adjusted to desired levels and heat-up of the liquid recycle stream was begun. The temperatures of the inlet and outlet streams of the cooling tower reached steady state values in about 30 min. At this time, the makeup flow rate was adjusted so that the makeup to blowdown ratio would be approximately that desired. (To simulate common industrial practice this ratio was usually kept near 10.) This period of adjustment usually took more than an hour to achieve due to the trial and error nature of setting the makeup flow rate to achieve a desired number of cycles of concentration.

After the desired number of cycles of concentration was approximately reached, a 2 mL sample of material was withdrawn from the sump and replaced with 2 mL of blowdown. This process was repeated about once per hour to give a series of samples whose composition would be an indicator of the approach to steady state conditions with respect to the organic contaminants in the wastewater. This procedure was changed after test No. 10 and samples were withdrawn from the composite blowdown collected over approximately one hour.

At the end of approximately 5 hours of operation, about 1/3 of the total gas flow from the cooling tower was diverted to the cold trap. Upstream of the cold trap, the gas passed through a condensor chilled with ice water. Condensate was collected in a trap and the gas then passed to the liquid nitrogen cooled impinger. The amount of material collected in the liquid nitrogen trap was approximately 1/8 the amount collected in the ice water trap. The trapping phase of the test lasted approximately 30 minutes. The test was terminated when water condensed in the cold trap froze to an extent sufficient to plug the trap inlet. Samples collected during the tests were refrigerated immediately after collection and remained under refrigeration until they were analyzed.

Organic compounds in the makeup, circulating water (i.e., sump or blowdown samples) and liquid condensed from the vapor phase were analyzed by direct injection gas chromatography. Details of the analytical procedure are given in Table 9. Ammonia analyses were conducted with an Orion selective ion electrode. Cyanide and thiocyanate analyses were done by wet chemistry according to Standard Methods (APHA, 1975).

Data pertaining to water and air temperature stability for selected tests are given in Appendix C. Once the temperatures came to steady state for a particular set of test conditions, fluctuations of more than ± 1° C were rare. The approach of organic compound recoveries to steady state over the course of the test is given in Appendix D. Calculations of the tower characteristic, a measure of cooling efficiency (commonly referred to as Merkel number in the cooling tower industry) for selected tests are given in Appendix E.

## 4.2 Major Component Recoveries in Cooling Tower Blowdown

Operating conditions and recoveries are given in Table 10. Recoveries are calculated from analyses of samples taken near the end of each test as

$$R_i = \frac{C_{Bi}}{C_{Fi}C} (100\%) \qquad (26)$$

## TABLE 9. ORGANIC ANALYTICAL TECHNIQUES

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### METHANOL, ACETONE, AND ACETONITRILE ANALYSIS

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Column - 80/120 Carbopack B AW/5% carbowax 20m

2m x 1/4" OD x 2 mm ID glass column

Detector - Flame ionization detector

Gas chromatograph - Perkin Elmer Sigma 10

Carrier Gas - Helium

Temperatures

- Column - isothermal at 40°C, 16°C/min to 130°C, hold 15 min.
- Injector - 220°C
- Detector - 250°C

Sample Size - 2 μL

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### PHENOL AND HYDANTOIN ANALYSIS

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Column - SE 54, 0.25 micron film thickness, 0.247 mm ID

Fused silica capillary column, 15 m (J&W)

Detector - Flame ionization detector

Gas chromatograph - Varian Model 3700

Recorder - Perkin Elmer Sigma 10

Carrier Gas - Helium

Temperatures

- Column - 50°C for 4 min., then heated to 230°C at 10°C/min. and held at 230°C for 10 min.
- Injector - 240°C
- Detector - 320°C

Sample Size - 0.2 μL sample injected, 10:1 split ratio

TABLE 10. FIVE CENTIMETER DIAMETER COOLING TOWER TEST OPERATING CONDITIONS AND COMPONENT RECOVERIES
(Simulated Pretreated Wastewater)

| Test | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Temperatures: | | | | | | | | |
| Gas In °C | 27 | 32 | 34* | 31* | 31 | 29 | 30 | 31 |
| Gas Out °C | 44 | 41 | 38 | 46 | 36 | 48 | 43 | 49 |
| Gas in Wet Bulb °C | 20 | 24 | 25 | 23 | 23 | 20 | 19 | 21 |
| Water In °C | 51 | 49 | 49 | 61 | 44 | 50 | 49 | 61 |
| Water Out °C | 24 | 23 | 20 | 22 | 19 | 35 | 27 | 27 |
| Liquid/Gas g/g | 1.23 | 1.32 | 1.20 | 1.20 | 1.20 | 2.40 | 1.20 | 1.20 |
| Cycles of Concentration | 11.5 | 8.6 | 11.4 | 9.4 | 10.1 | 7.9 | 8.4 | 9.0 |
| Circulation Rate mL/sec $cm^2$ | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 |
| Gas Flow Rate g/sec $cm^2$ | 0.021 | 0.020 | 0.021 | 0.021 | 0.021 | 0.011 | 0.021 | 0.021 |
| Blowdown Recoveries (%) | | | | | | | | |
| Water | 8.7 | 12.0 | 8.8 | 10.6 | 9.9 | 12.7 | 12.0 | 11.1 |
| Phenol | 7.0 | NA | 8.6 | 10.7 | 10.0 | 9.0 | 10.2** | 9.6** |
| Hydantoin | 30. | NA | 34. | 23. | 15. | 28. | 50. | 23. |
| Methanol | 0.5 | 0.8 | 1.1 | 1.1 | 0.8 | 0.9 | 1.1 | 0.5 |
| Acetone | 0 | 0.4 | 0 | 0.8 | 0 | 0 | 0 | 0 |
| Ammonia | NA | NA | 8.2 | NA | NA | 3.6 | 3.9 | 0.5 |
| Cyanide | NA | NA | 2.7 | NA | NA | NA | NA | NA |
| Thiocyanate | NA | NA | 36. | NA | NA | NA | NA | NA |

* Nitrogen used instead of air

** Phenol doubled in makeup

NA = not analyzed

### TABLE 10. FIVE CENTIMETER DIAMETER COOLING TOWER TEST OPERATING CONDITIONS AND COMPONENT RECOVERIES - (continued)
(Simulated Pretreated Wastewater)

| Test | 9 | 10 | 11 | 12 | 13 | 14 | 15*** | 16*** | 17*** |
|---|---|---|---|---|---|---|---|---|---|
| Temperatures: | | | | | | | | | |
| Gas In °C | 31 | 31 | 30 | 30 | 29 | 32 | 29 | 30 | 29 |
| Gas Out °C | 43 | 43 | 38 | 42 | 39 | 40 | 38 | 38 | 39 |
| Gas in Wet Bulb °C | 20 | 19 | 20 | 19 | 19 | 22 | 20 | 21 | 21 |
| Water In °C | 50 | 50 | 50 | 61 | 50 | 50 | 50 | 50 | 50 |
| Water Out °C | 26 | 27 | 23 | 23 | 25 | 26 | 24 | 26 | 27 |
| Liquid/Gas g/g | 1.20 | 1.20 | 0.82 | 0.82 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 |
| Cycles of Concentration | 2.7 | 9.8 | 10.3 | 11.2 | 1.8 | 12.8 | 10.9 | 10.2 | 7.8 |
| Circulation Rate mL/sec $cm^2$ | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 | 0.026 |
| Gas Flow Rate g/sec $cm^2$ | 0.021 | 0.021 | 0.031 | 0.031 | 0.021 | 0.021 | 0.021 | 0.021 | 0.021 |
| Blowdown Recoveries (%) | | | | | | | | | |
| Water | 33.7 | 10.2 | 9.7 | 8.9 | 56.2 | 7.8 | 9.1 | 9.8 | 12.9 |
| Phenol | 30.4 | 8.7 | 7.9 | 6.7 | 13.5 | 4.8 | 7.3 | 11.0 | 15.4 |
| Hydantoin | 52.0 | 26. | 14. | NA | NA | 12.6 | 27. | 34. | 41.9 |
| Methanol | 3.7 | 1.0 | 0.7 | 0.8 | 11. | 0.8 | 0.9 | 0.8 | 1.4 |
| Acetone | 0 | 0 | 0 | 7.2 | 6.2 | 1.8 | 0.9 | 0 | 0 |
| Ammonia | 9.3 | 25. | 6.2 | NA | 66. | 36. | 22. | NA | 15. |
| Cyanide | NA | NA | NA | NA | 13. | NA | 1.7 | NA | 6.0 |
| Thiocyanate | 74. | 30. | 30. | NA | 100. | NA | 24. | NA | NA |

*** Bioactivity promoted

NA = not analyzed

where $R_i$ = percentage of component i recovered
$C_{Bi}$ = blowdown concentration of component i (mg/L)
$C_{Fi}$ = feed (i.e., makeup) concentration of component i (mg/L)
$C$ = cycles of concentration, the ratio of makeup flow rate to blowdown flow rate.

The above definition of C neglects drift because the volume of drift generated in the laboratory cooling tower was too low to measure. Recoveries are calculated from analysis of samples taken after a volume of makeup equal to at least three times the volume of the liquid in the system had been added. This volume is counted from the time that the column reached approximate steady state with regard to temperature.

In the course of the study, the effects of the independent variables; cycles of concentration, liquid/gas ratio, inlet water temperature, phenol concentration, and bioactivity were investigated. The most significant operating variable in terms of recovery of phenol was cycles of concentration, C. Lower cycles of concentration imply less residence time on the packing and less air/water contact for any individual portion of the cooling water. As a result, the concentration of contaminants circulating in the column and the concentration of contaminants in the blowdown overflowing from the column sump were higher. It was observed that for low cycles of concentration (Tests 9 and 13), phenol recoveries were much higher, although for more volatile (i.e., higher vapor pressure) components (methanol and acetone), even the much shorter residence time was sufficient for nearly complete evaporation. The evaporation of the contaminants in the cooling tower is linked to the volatility of these contaminants relative to water. Apparent vapor pressures (calculated by multiplying reported vapor pressures for pure components by infinite dilution activity coefficients) are shown in Table 5 as $\gamma_s P_s$ along with relative volatilities. Acetone, for example, is approximately 37 times as volatile as water in terms of apparent vapor pressure (i.e., vapor pressure times activity coefficient) and may be essentially completely removed in one pass through the column.

At a given number of cycles of concentration, changes in liquid-to-gas ratio $(L'/G')$ and inlet water temperature $T_1$, had no significant effect on recovery of volatile components in the blowdown. This can be explained in terms of the driving force for contaminant volatilization relative to that for evaporation of water. At a constant temperature, the contaminant and water will volatilize in proportion to their apparent vapor pressures since the driving force for mass transfer is:

$$P_v - P_v^*$$

where $P_v^*$ is the equilibrium partial pressure of the contaminant at a given temperature. Thus, when the cycles of concentration is fixed, the proportion of the contaminant to be evaporated is also fixed, although the time required for these changes to take place will vary with liquid flowrate and $L'/G'$. Similarly although the vapor pressure of water and the contaminants will both change with temperature, the ratio of the vapor pressures will be approximately constant over the range of typical cooling tower operating conditions. The ratio of mass transfer rates of water and the contaminant will be approximately equal even if the water temperature is increased (making the rate of evaporation of both water and the contaminant higher) or decreased.

Since cycles of concentration will typically be fixed by the desired water balance for the overall plant (i.e., maximum water reuse for conservation and because of higher costs associated with treatment of blowdown prior to discharge) changing cooling tower operating conditions is not a feasible way to reduce plant emissions. The emissions may, however, be controlled by increasing or decreasing the level of pretreatment to which the tower makeup is subjected. In order to test this effect, the feed to the cooling tower for tests 7 and 8 contained twice the concentration of phenol as the other tests (i.e., 320 mg/L versus 160 mg/L). All other components were added in the usual amounts (see Table 8). In tests 7 and 8, the concentrations of phenol in the blowdown approximately doubled, i.e., the percent phenol recovered was unchanged. At the tested level the increased phenol concentration did not have a significant effect on the recoveries of methanol and acetone.

Of particular interest are the tests conducted with nitrogen rather than air in the cooling tower. In these cases, biological oxidation as well as chemical oxidation was eliminated as a possible removal mechanism for contaminants. The results of tests 3 and 4 show approximately the same recoveries of organics in the blowdown as those tests where air was used at approximately the same cycles of concentration. While this does not discount the potential of biological oxidation as a means of pollutant destruction in cooling towers, it does show that the disappearance of volatile contaminants takes place even in the absence of oxygen. Thus, the possibility exists that an upset in a cooling tower with demonstrated high levels of biological oxidation could take place resulting in greatly reduced bioactivity without any noticeable change in the composition of the circulating water.

The first 14 tests were conducted with no attempt made to promote bioactivity. In particular, the first 14 tests were run intermittently and following each test (which lasted approximately eight hours) the flows of water and air were stopped and the packing was permitted to dry. No phosphorus was present in the feed to the column, (which is needed for biological growth) and throughout the testing period of approximately nine months, no biological growth was macroscopically visible on the packing.

Following test 14, the flow of both air and water was continuously maintained. Eleven days elapsed between tests 14 and 15. The column was seeded with some feed solution which had been left in a large open beaker and showed visible signs of bioactivity. In addition, phosphoric acid was added to the column makeup to prevent a lack of phosphorus from limiting growth (i.e., N:P<10). (The addition of this small volume of acid did not change the pH, thus ammonia and cyanide volatilities were unchanged.) Biological growth built up on the packing and walls of the column until the column was shut down after the third bioactive test (Test 17).

For tests 15, 16, and 17, an effort was made to promote bioactivity. These tests were conducted with visible growth on the packing and walls of the column. No significant difference was observed in recoveries of contaminants with the bioactive column. It is not possible on this basis, to say that biological oxidation was not occurring since biological oxidation could compete with the stripping mechanism which might result in no net change in blowdown recoveries. It is unlikely, however, that under the conditions of the tests, biological oxidation could be rapid enough to remove more than a small fraction of the contaminants which were removed by non-biological mechanisms.

After the conclusion of the simulated pretreated wastewater tests the feed to the 5 cm diameter laboratory cooling tower was switched to extracted stripped gas liquor obtained from the University of North Dakota Energy Research Center (UNDERC). This sample was shipped by air and received at RTI on March 20, 1984. The sample was stored under refrigeration at 4°C in 5 gallon polyethylene containers. Aliquots were withdrawn as needed. The column was operated for 18 days with continuous liquid and gas flow. During this period, biological growth increased visibly on the packing as well as the walls of the column. The only interruption that occurred was an eight hour period in which the first test was conducted with nitrogen instead of air. Biological growth was present but presumably inactive during the nitrogen test.

Two tests were conducted; Test 18, using nitrogen gas instead of air and Test 19, conducted in a similar manner with air. Feed concentrations of the UNDERC wastewater are given in Table 11. These data are the average from the analyses of fresh feed samples used in the two tests. The concentrations are quite close to those in the earlier synthetic wastewater tests with the exception of hydantoin, which was about three times higher in the UNDERC water.

The UNDERC wastewater contained alkyl hydantoins and hydantanoic acid (Mohr, et al., 1983; Wiltsee, 1984) and little or none of the parent compound hydantoin. The analysis reported in Table 11 treats these substituted hydantoin compounds as the parent compound, i.e., the chromatographic analysis was based on a standard curve prepared from hydantoin, and area ratios for the window of hydantoin retention times were used to calculate concentrations. This procedure should yield accurate percent recoveries of the hydantoin group owing to the cancellation of errors which may result from differences in chromatographic response factors between hydantoin and substituted hydantoins (in other words, the concentration of makeup and blowdown samples used in equation 26 would be inflated by a constant factor) assuming that the rates of disappearance of the different hydantoin compounds in the tower do not vary greatly.

Test operating data and results are shown in Table 12. These two tests were conducted in a similar manner to each other, with the only intentional variation being the substitution of nitrogen for air in test 18. The other slight differences in operation between the tests were the use of slightly hotter, drier inlet gas and a slightly lower number of

## TABLE 11. COMPOSITION OF UNDERC EXTRACTED STRIPPED GAS LIQUOR USED IN THE RTI 5 CENTIMETER DIAMETER COOLING TOWER TESTS

| Component | Concentration (mg/L) |
|---|---|
| Hydantoin | 7460 |
| Ammonia | 480 |
| Methanol | 250 |
| Phenol | 220 |
| Acetone | 23 |
| Acetonitrile | 2.5 |

Note: Approximately 100 mg/L phosphorus was added in the form of phosphoric acid to promote biological growth.

## TABLE 12. DESCRIPTION AND RESULTS OF FIVE CENTIMETER DIAMETER COOLING TOWER TESTS CONDUCTED WITH UNDERC EXTRACTED STRIPPED GAS LIQUOR

| Test | 18 | 19 |
|---|---|---|
| Gas | Nitrogen | Air |
| Temperatures: | | |
| Gas In °C | 29 | 30 |
| Gas Out °C | 39 | 39 |
| Gas in Wet Bulb °C | 21 | 21 |
| Water In °C | 50 | 50 |
| Water Out °C | 25 | 25 |
| Liquid/Gas g/g | 1.20 | 1.20 |
| Cycles of Concentration | 11.9 | 10.9 |
| Circulation Rate mL/sec $cm^2$ | 0.026 | 0.026 |
| Gas Flow Rate g/sec $cm^2$ | 0.021 | 0.021 |
| Blowdown Recoveries (%) | | |
| Water | 8.5 | 9.2 |
| Phenol | 3.4 | 5.6 |
| Hydantoin | 24-41 | 29.5 |
| Methanol | 1.1 | 0.9 |
| Acetone | 10.3 | 5.1 |
| Acetonitrile | 12.9 | 9.2 |
| Ammonia | 23.1 | NA |
| Cyanide | 32.7 | NA |
| Thiocyanate | NA | NA |

NA = not analyzed

cycles of concentration in test 19. These factors combined resulted in a higher makeup flow rate in test 19. Temperature profiles for the tests are shown in Appendix C. Concentration data taken over the course of the tests are given in Appendix D.

Within the accuracy of chemical analyses, recoveries in the blowdown for the organic components in the wastewater were not affected by the absence of oxygen in the inlet gas. Thus, although the column was bioactive, suppression of bioactivity through the use of nitrogen instead of air did not result in a significant increase in the recovery of organics in the blowdown. Bioactivity in the column was confirmed by the accumulation of slime on the packing and walls of the column during the acclimation period and by a total plate count of organisms in the liquid in the tower sump at the conclusion of the tests. The liquid showed an organism count of >300,000/100 mL. This is not a particularly high level of organisms but since the bulk of the biological oxidation is carried out by fixed film organisms on the packing surfaces (by analogy to trickling filters used for treatment of municipal and industrial wastewater) rather than suspended organisms in the sump, the potential for biological oxidation may still be important.

The consistency of the recovery of organics in the blowdown in the absence and presence of bioactivity cannot necessarily be taken to mean that bioactivity cannot under some circumstances contribute to the removal of organics from the liquid in the tower. The air stripping of compounds in the tower is dependent upon the concentration in the liquid (as was demonstrated in the earlier experiments with synthetic pretreated wastewater). It was observed that when the concentration of phenol in the makeup was doubled the same fractional recovery of phenol was obtained (i.e., twice as much phenol was stripped on a mass basis). In analogous way, the absence of biological oxidation in the tower can be viewed as increasing the driving force for air stripping.

The conclusion from the preceding argument is that even though no difference was observed in recovery of organics in the presence and absence of bioactivity, it cannot be proven that none of the organics were removed by biological oxidation. Attempts to recover organics from the vapor leaving the tower and thus confirm the removal mechansism are described in Section 4.4. Predictions of the extent of biological oxidation based on bio-kinetic data for phenol have been made in Section 3.

These calculations indicate that for a compound such as phenol, the presence or absence of bioactivity will result in a difference of less than 10% in mass emissions to the air for the RTI five centimeter diameter laboratory cooling tower. In addition, for more volatile (i.e., higher vapor pressure, more susceptible to air stripping) compounds such as acetone, acetonitrile and methanol, biological oxidation would have a much less important effect (assuming that these compounds are equal to phenol in biodegradability).

## 4.3 Recoveries of Other Components in the Cooling Tower Blowdown

Additional chemical analyses were conducted for selected samples. Acetonitrile, added to the synthetic wastewater solution at 2 mg/L in tests 1 through 17, and present in the UNDERC stripped gas liquor used for tests 18 and 19 at 2.5 mg/L bordered on the detection limit which was typically 0.5 to 1.0 mg/L. Where this compound was detectable in blowdown and sump samples, recoveries were consistently below 10% for tests 1 through 17. Recoveries of 12.9 and 9.2% were found in tests 18 and 19.

Cyanide and thiocyanate were analyzed in selected feed and blowdown and sump samples. Recoveries are given in Table 13. Most notable among the cyanide data is the recovery in the blowdown of 33% of the cyanide present in the UNDERC extracted stripped gas liquor as feed for this test. This was a far greater recovery than that found in any of the tests conducted with synthetic feed. (Cyanide recovery in test 13 was 13%; this test was conducted at 1.8 cycles of concentration and the recoveries of all components during this test were much higher than the average recoveries for tests conducted at approximately ten cycles of concentration.) The 33% recovery with UNDERC stripped gas liquor is still lower than the 58% recovery reported by Willson et al., (1983) in a test at UNDERC at 9.2 cycles of concentration with similar makeup water.

The pH of the blowdown from the RTI tests with UNDERC extracted stripped gas liquor was approximately 7.0 in comparison to 8.0 reported by Willson, et al., (1983) for tests with similar feed. The slightly less basic solution in the RTI tests would favor greater cyanide volatility and may partially explain the lower recovery of cyanide in the RTI tests relative to the tests at UNDERC. The pH of the blowdown from the RTI tests with simulated extracted, stripped wastewater was also approximately 7.0. In general, as the pH of the circulating cooling water decreases, greater rates of stripping would be expected. The lower pH in the RTI tests would not, in the absence of other ions, be sufficient to explain the difference in cyanide recoveries, because the hydrogen cyanide would be essentially completely dissociated in either case. Other chemical species present in the UNDERC extracted, stripped gas liquor may have decreased the vapor pressure of HCN.

The tests for which thiocyanate analyses were conducted produced thiocyanate recoveries in the range of 24-36% except for the low cycles of concentration tests, 9 and 13. If thiocyanate were nonvolatile, recoveries close to 100% would be expected. The low recoveries of thiocyanate may be due to decomposition to cyanide in the cooling tower, followed by stripping of the products of decomposition. The rates of both the hydrolysis and the oxidation reactions would generally be very low at near neutral pH. In coal gasification and coke manufacturing wastewaters, thiocyanate is formed by aqueous phase reactions of cyanide and sulfide (Nakles, 1979). No sulfide was present in the simulated wastewater and the formation reactions may be reversed to some extent.

TABLE 13. CYANIDE AND THIOCYANATE RECOVERIES IN FIVE CENTIMETER DIAMETER COOLING TOWER TESTS

| Test | Recovery in Blowdown (%) | |
|---|---|---|
| | Cyanide | Thiocyanate |
| 3 | 2.7 | 36 |
| 9 | NA | 74 |
| 10 | NA | 30 |
| 11 | NA | 30 |
| 13 | 13. | 100 |
| 15 | 1.7 | 24 |
| 17 | 6.0 | NA |
| 18 | 33. | NA |

NA = not analyzed

Thiocyanate is readily biodegradable but the low recoveries of thiocyanate in the tower blowdown occurred in tests where bioactivity was not promoted including test 3 in which nitrogen was used in place of air.

### 4.4 Vapor Sampling

In order to establish the fate of the components which were not recovered in the tower blowdown, attempts were made to measure the flow of these components in the vapor leaving the top of the tower. Samples taken from the condenser and liquid nitrogen cooled trap were analyzed for organics using the methods of Table 9. The results of these analyses were extremely erratic and were not reproducible from test to test. The tentative explanation for these problems is that sampling procedures were not adequate to insure quantitative recovery of the components from the gas stream. This was possibly due to inadequate residence time in the condenser (indicated by incomplete recovery of evaporated water). In addition, material collected in the liquid nitrogen trap may have been restripped after the sampling period when a small volume of air which was liquified in the trap reevaporated. For these reasons, mass balance closures could not be achieved for methanol and acetone. Mass balance closures for phenol were erratic and varied between 25 and 1000%. The reasons for over recovery of phenol may be absorption of vapor phase phenol by water droplets in the sampling lines prior to commencement of sampling. Qualitatively, the presence of phenol and hydantoin was consistently confirmed in the vapor phase effluent from the column.

In an attempt to improve mass balances, an impinger system was used to sample the exit gas stream from the column in tests 17-19 In these tests a metered split stream of the exit gas stream was directed through impingers containing 1 N $H_2SO_4$ and 1 N NaOH. The volume of each impinger solution was measured with a graduated cylinder (impinger solution volumes ranged from 40 to 60 mL). The impinger solutions were then analyzed by the same methods as the other samples. This sampling method was slightly better than the condenser/cold trap method used in earlier tests. Mass balances for tests 17-19 are given in Tables 14-16. Methanol mass balance closure varied from 1.8 to 46% for three tests. Ammonia mass balance closure totaled 37% and 70% for two tests. The likely cause of the incomplete closure of these components is that they were incompletely trapped in the impingers. The excess mass balance closure for phenol in

### TABLE 14. MASS BALANCE (mg/min) IN FIVE CENTIMETER TOWER WITH SIMULATED WASTEWATER AT 7.8 CYCLES OF CONCENTRATION

| | Methanol | Ammonia | Cyanide |
|---|---|---|---|
| In: Makeup | 0.332 | 0.665 | 0.0429 |
| Out: Blowdown | 0.004 | 0.0875 | 0.00257 |
| acid scrubber | 0.066 | 0.366 | ------- |
| base scrubber | ----- | ------ | 0.00633 |
| TOTAL | .070 | 0.464 | 0.00890 |
| Recovery | 21.1% | 69.8% | 20.8% |

### TABLE 15. TEST 18: MASS BALANCE (mg/min) IN FIVE CENTIMETER TOWER WITH UNDERC EXTRACTED STRIPPED GAS LIQUOR AT 11.9 CYCLES OF CONCENTRATION (NITROGEN USED)

| | Phenol | Methanol | Ammonia | Cyanide |
|---|---|---|---|---|
| In: Makeup | .298 | .339 | .650 | .00102 |
| Out: | | | | |
| Blowdown | .010 | .004 | .150 | .00033 |
| Acid scrubber | ---- | .002 | .093 | ------ |
| Base scrubber | .517 | ---- | ---- | <.002 |
| TOTAL | .527 | .006 | .243 | <.00233 |
| Recovery | 177% | 1.8% | 37% | <228% |

## TABLE 16. TEST 19: METHANOL MASS BALANCE (mg/min) IN FIVE CENTIMETER TOWER WITH UNDERC EXTRACTED STRIPPED GAS LIQUOR AT 10.9 CYCLES OF CONCENTRATION

| | | |
|---|---|---|
| In: | Makeup | .373 |
| Out: | | |
| | Blowdown | .004 |
| | Acid Scrubber | .169 |
| | TOTAL | .173 |
| Recovery | | 46% |

test 18 may have been due to analytical error, or an inaccuracy in the metering of the gas which passed through the impinger. One source of analytical error may be a difference in chromatographic response for alkaline impinger solution and the relatively neutral standards used for instrument calibration.

Hydantoin being neither strongly acidic or strongly basic was not analyzed in the impinger solutions. The response to hydantoin at low levels, (>100 mg/L) was not reliable and even if it was completely removed from gas stream, measurements of this component would not be meaningful. Phenol was detected only in the impinger from test 18 due to analytical problems resulting in a lack of sensitivity for the other tests. Ammonia and cyanide analyses were not attempted for the impingers from test 19. Mass balances are reported in mg/min for the steady state period when the impinger samples were taken.

While the failure to quantitatively recover the contaminants removed from the liquid phase of the cooling tower in vapor phase samples leaves open the possibility that some of these materials may have been chemically or biologically decomposed in the liquid phase, other evidence suggests that these mechanisms are of minor importance. In particular, the substitution of nitrogen for air in some of the tests did not affect the concentration of the circulating liquid phase. In addition, operation of the column to promote biological activity did not decrease the concentration of the contaminants in the circulating liquid phase from that of the tests when biological activity was not promoted. The chromatograms obtained contained a significant amount of noise for retention times other than those corresponding to the compounds of interest. This noise was not of sufficient magnitude to impair the analysis of compounds known to be present in the influent but it was impossible to attribute random chromatogram peaks to the production of reaction intermediates which may have been present in blowdown samples at low levels.

### 4.5 Application of the Model to the Five Centimeter Diameter Cooling Tower

The cooling tower model was applied to the five centimeter diameter laboratory cooling tower. Typical output from the model is shown in Table 17. This table shows model predictions of the fate of phenol at 10 cycles of concentration under bioactive conditions. Additional model

## TABLE 17. MODEL OUTPUT: THE FATE OF PHENOL IN THE FIVE CENTIMETER LABORATORY COOLING TOWER AT 10 CYCLES OF CONCENTRATION

```
Liquid Streams
    Makeup
        Flow rate:      7.71       lb/(sq ft hr)
                        0.168      lb/hr
        Pollutant Conc:      150.  ppm
    Circulation
        Flow Rate:      190.       lb/(sq. ft hr)
                          4.15     lb/hr
        Inlet of cooling tower
            Pollutant conc:      46.7 mg/L
            Biomass conc:       492.  mg/L
            Temperature:        122.00 F
        Outlet of cooling tower
            Pollutant conc:      42.4 mg/L
            Biomass conc:       512.  mg/L
            Temperature:         79.42 F
            Oxygen conc:          8.12 ppm
        Heat duty:      176.5      Btu/hr
        Oxygen Conc at holding basin outlet:     7.66 ppm
    Drift
        Flow rate:      0.950E-011b/(sq ft hr)
                        0.207E-02 lb/hr
        Pollutant conc:      46.7 ppm
        Pollutant emission: 0.968E-07 lb/hr
                            0.575E-06 lb/lb makeup
        Biomass conc:       492.  ppm
        Biomass emission:    0.102E-05 lb/hr
                             0.606E-05 lb/lb makeup
    Blowdown
        Flow rate:      0.676      lb/(sq ft hr)
                        0.147E-01 lb/hr
        Pollutant conc:      46.7 ppm
        Pollutant blowdown:  0.689E-06 lb/hr
                             0.409E-05 lb/lb makeup
        Biomass conc:       492.  ppm
        Biomass blowdown:    0.725E-05 lb/hr
                             0.431E-04 lb/lb makeup
 Gas stream
    Flow rate:      157.       lb/(sq ft hr)
                      3.43     lb/hr
    Pollutant conc:     0.962      ppmv
    Pollutant emission: 0.117E-04 lb/hr
                        0.693E-04 lb/lb makeup
 Emissions Summary
    % of pollutant report to blowdown:                       2.73
    % pollutant stripped:                                   46.19
    % pollutant evolved with drift:                          0.38
    Total % of pollutant emitted to atmosphere:             46.57
    % pollutant biooxidized:                                50.70
    % pollutant biooxidized in tower:                       49.81
    Emissions of bioactive material:   0.4038E-01
     (lb/lb pollutant in makeup)
```

predictions at varying cycles of concentration under sterile and bioactive conditions are given in Table 18. The importance of bioactivity in the removal of phenol from the cooling tower is increased because of the very high specific surface area of the column packing. Under sterile conditions predictions of phenol removal are very close to actual laboratory observations. Under bioactive conditions the model predicts a greater degree of phenol removal than that observed in the laboratory tests. Additional model runs were made to predict the fate of methanol in the five cm. diameter column. For operation at ten cycles of concentration these predictions are given in Table 19.

The sensitivity of phenol removal to changes in operating conditions at ten cycles of concentration under bioactive conditions was determined. In the base case, about 47% of the influent phenol was emitted due to stripping and drift. If the phenol concentration in the makeup were doubled (i.e., from 150 mg/L to 300 mg/L) approximately 52% of the phenol would be emitted to the atmosphere. (This implies that a 100% increase in phenol concentration in the makeup would result in a 121% increase in phenol emissions.) If the liquid circulation rate were doubled (i.e., from 1.55 to 3.1 $g/cm^2$ min) approximately 58% of the phenol would be emitted. Experimental data are shown along with model predictions in Figure 3.

The small but consistent excess of predicted emissions relative to observed emissions is possibly due to the fact that makeup to the five centimeter cooling tower was added to the sump to insure adequate mixing. The model assumes normal industrial practice of adding makeup water at the top of the tower.

## TABLE 18. MODEL PREDICTIONS: FATE OF PHENOL IN RTI FIVE CENTIMETER DIAMETER COOLING TOWER BASE CASE

| Cycles of Concentration | Removal Mechanism<br>Blowdown | Stripping | Drift | Biooxidation |
|---|---|---|---|---|
| | % Removal | | | |
| Bioactive | | | | |
| 5 | 6.6 | 46 | 0.38 | 47 |
| 10 | 2.7 | 46 | 0.38 | 51 |
| 15 | 1.6 | 46 | 0.38 | 53 |
| 20 | 1.0 | 45 | 0.37 | 54 |
| 25 | 0.74 | 44 | 0.36 | 55 |
| Sterile | | | | |
| 5 | 12. | 87 | 0.71 | -- |
| 10 | 5.5 | 94 | 0.77 | -- |
| 15 | 3.3 | 96 | 0.78 | -- |
| 20 | 2.3 | 97 | 0.79 | -- |
| 25 | 1.6 | 98 | 0.80 | -- |

-- = not applicable

## TABLE 19. PREDICTIONS OF METHANOL DISTRIBUTION IN THE FIVE CENTIMETER DIAMETER COOLING TOWER AT TEN CYCLES OF CONCENTRATION

| | Percent Removal<br>Sterile | Bioactive |
|---|---|---|
| Stripping | 98.3 | 75.3 |
| Blowdown | 1.5 | 1.2 |
| Drift | 0.2 | 0.2 |
| Biological Oxidation | ---- | 23.3 |

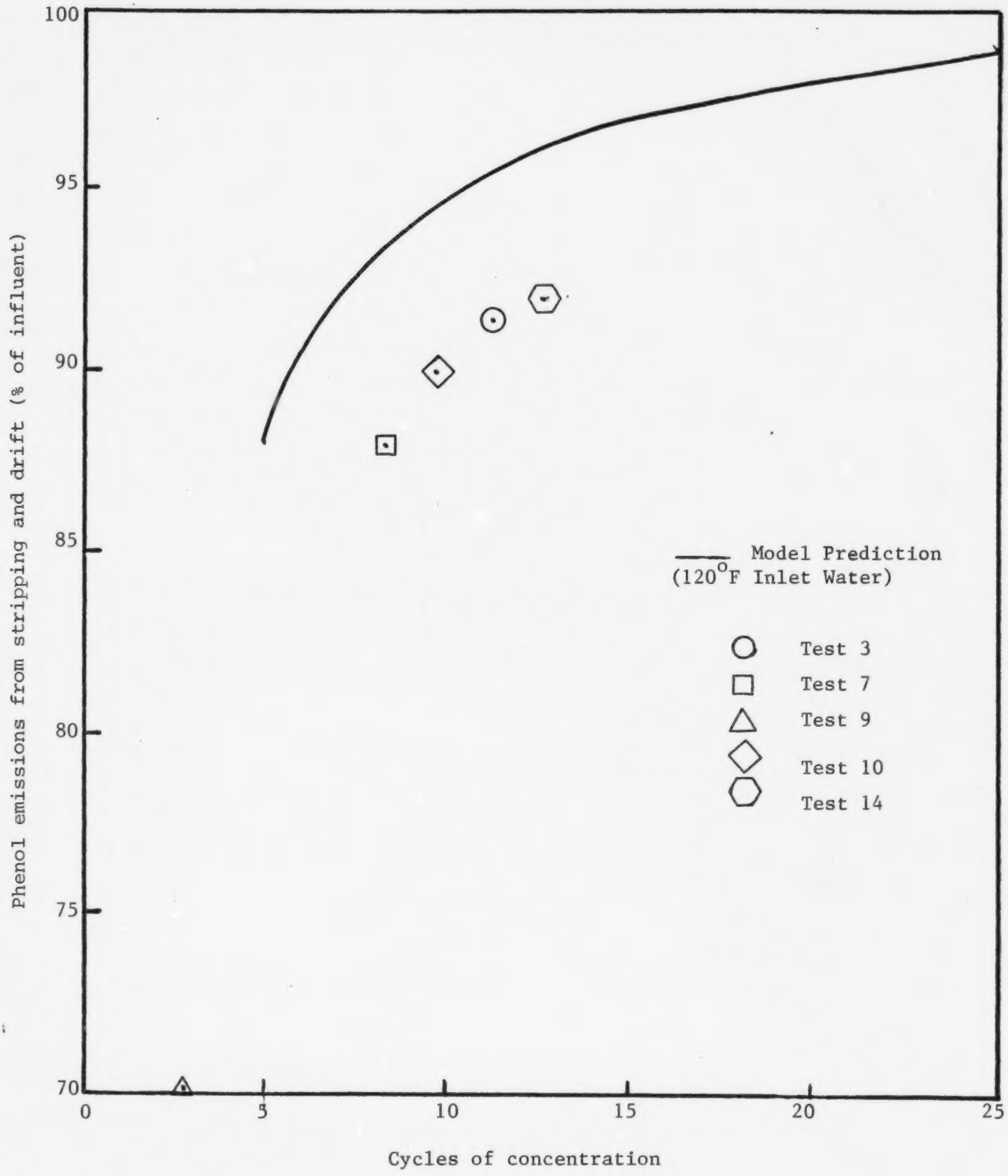

Figure 3. Predicted and experimentally observed emissions of phenol from the five centimeter laboratory cooling tower assuming sterile conditions. (Data from Table 10).

# 5.0 EXPERIMENTAL VALIDATION OF THE MATHEMATICAL MODEL USING A THIRTY CENTIMETER SQUARE BY NINETY-ONE CENTIMETER LABORATORY TOWER

## 5.1 Equipment and Procedure

The five-centimeter diameter laboratory cooling tower, described in Section 4, had the advantage of precise controllability of inlet air temperature and humidity and the capability of operation with nitrogen instead of air. There were, however, several disadvantages to the system. The packing, berl saddles, was not representative of cooling tower packing and had a relatively high pressure drop; as a result liquid and gas velocities through the column were restricted to lower than typical cooling tower rates.

A larger, thirty centimeter square, counterflow cooling tower was built to permit operation with packing representative of that used in industrial cooling towers and at liquid and gas velocities more representative of industry practice. The thirty centimeter square cooling tower system is shown in Figure 4. A detailed drawing of the tower is shown in Figure 5. The packing material consists of three thirty centimeter cubes of corrugated polyvinyl chloride sheeting supplied by the Munters Corporation (Fort Myers, FL) for use in full-scale industrial cooling towers. The packing is stacked vertically within a Plexiglass cooling tower with interior cross section of 30 cm square.

Water is circulated through the system with a Horizon Model VI-7135-25 centrifugal chemical feed pump. A heat load is imposed on the water as it is recirculated from the sump at the bottom of the cooling tower to a spray nozzle located above the packing. The heat is added as the water flows through a flanged stainless steel pipe containing a 6000 watt water heater element. The element flange is sealed to the pipe flange with an O-ring secured by four bolts. Inlet and outlet fittings are welded to the pipe wall. A type K thermocouple inserted into the downstream end of the pipe is used in a proportional control loop with a Research Incorporated Model 646 Phaser Power Controller of 50 Amp capacity. The heated water flows through a Spraying Systems #1/2 GG16 spray nozzle mounted above the packing. The nozzle is designed to produce a "full cone" spray pattern. A reasonably even distribution is achieved over the top of the

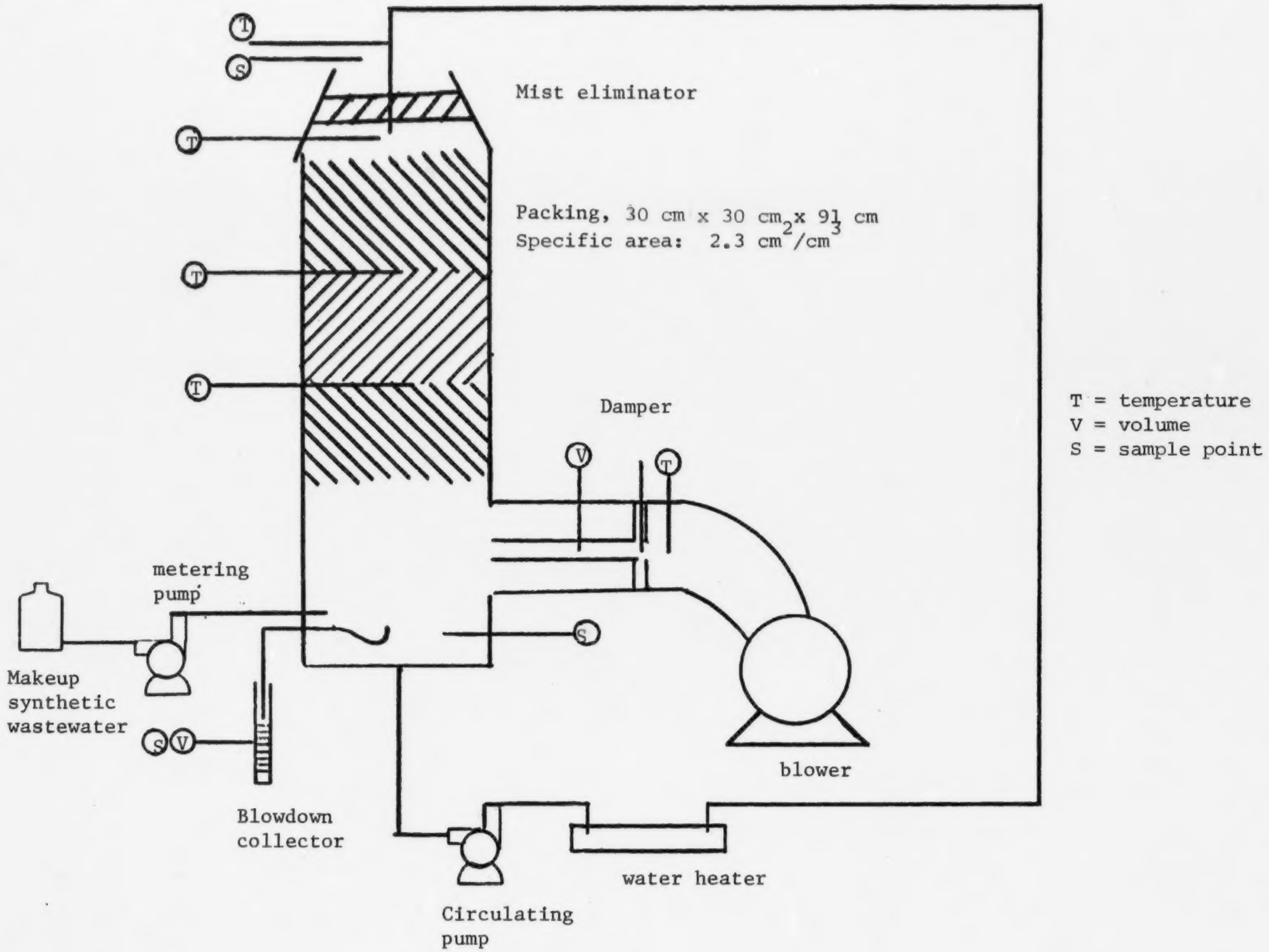
T
S
T
T
T
Mist eliminator
Packing, 30 cm x 30 cm x 91 cm
Specific area: 2.3 cm2/cm3
Damper
V
T
S
metering pump
Makeup synthetic wastewater
S V
Blowdown collector
blower
Circulating pump
water heater
T = temperature
V = volume
S = sample point

Figure 4. Thirty centimeter square cooling tower.system

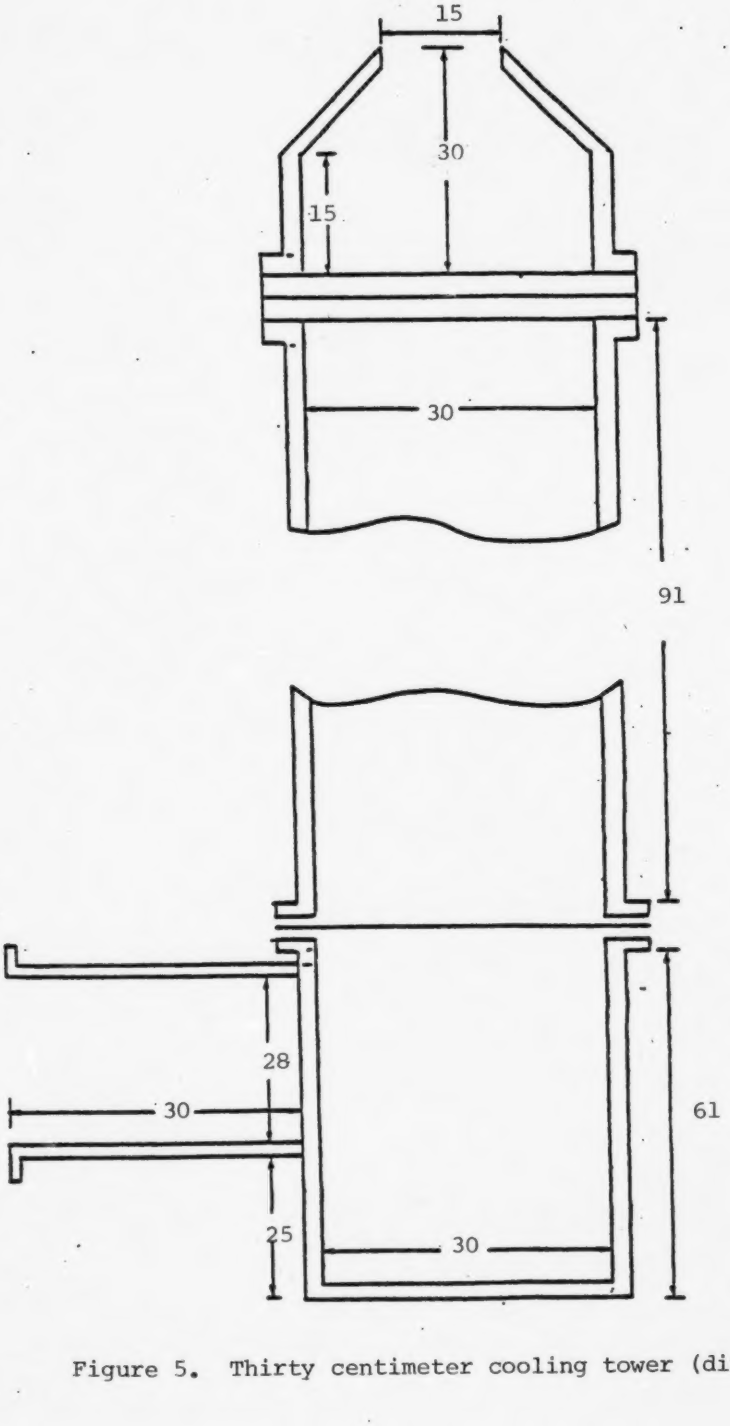
15
30
15
30
91
28
30
61
25
30

Figure 5. Thirty centimeter cooling tower (dimensions in cm).

uppermost packing cube. The distribution is improved by alternating flow patterns among the three packing cubes.

Air is supplied to the tower with a Dayton Model 7C453 blower. The air flow rate is adjusted with a sliding damper in the duct connecting the blower to the cooling tower. Air flow rates are measured by inserting a Flow Technologies electronic anemometer through an opening in the 5 cm duct and averaging readings taken at five positions. The damper is adjusted to produce the desired air flow rate. Temperature and relative humidity of the air are not controlled but measured and recorded at hourly intervals. Air flows out the top of the tower, which is reduced in cross sectional area from 30 cm square to 20 cm square at the exit. A mist eliminator of stainless steel wool is inserted in the cooling tower exit section approximately 8 cm above the spray nozzle. (This mist eliminator was removed for one test to permit collection of a small amount of drift.)

Makeup is added to the cooling tower sump from a 110 L stainless steel tank using a Milton-Roy Model MAI-34-95 adjustable stroke packed plunger metering pump. The makeup is added at a rate selected to achieve the desired cycles of concentration. Blowdown is removed through an overflow tube in the cooling tower sump. Blowdown flow rate is monitored by allowing this tube to discharge into a graudated cylinder.

Temperatures are measured in the cooling tower sump, directly above the nozzle, in the spray between the nozzle and the top of the packing, at 30 cm packing depth, at 61 cm packing depth, and in the ambient air at the blower intake. Liquid samples of feed and blowdown are taken. In addition, samples of gas leaving the cooling tower are taken by drawing a measured volume of gas through acid, base and water impingers. Water circulation rate was maintained at 4.3 liters/min (1.1 GPM) for all tests. This flow rate was measured volumetrically and resulted in a liquid loading rate of 0.075 mL/sec $cm^2$.

The feed solution used had the same composition as the simulated pretreated wastewater used in the tests in the five cm laboratory cooling tower (given in Table 8). In addition, 25 mg/L of chloride was added (in the form of sodium chloride). The synthetic feed solution was prepared in 76 or 110 L batchs and used within 24 hours of preparation. Typically, two or three sets of experimental conditions were achieved in one continuous run on a given day.

The experimental procedure used for tests in the 30 cm square tower was similar to that of the earlier tests in the 5 cm diameter column. The first samples were taken after approximately four hours. Additional samples were taken after two more hours. Following this, the makeup rate was adjusted to yield a different cylces of concentration. Sampling at the new conditions was done after two more hours. Chemical analyses were carried out as in the earlier tests (See Section 4).

A total of twelve tests were conducted. The first ten tests were conducted to confirm the influence of liquid to gas ratio and cycles of concentration. One test, L-11, was conducted to determine the influence of common cooling tower additives on emissions. This test was conducted with the same basic makeup composition as the other tests, but in addition, 10 mg/L of Calgon CL-37 antifoam, 10 mg/L of sodium metaphosphate and 28 mg/L of potassium dichromate were added (76 L of the makeup water were prepared). Following test L-11, the tower was drained and rinsed. A fresh batch of makeup solution was prepared and water was circulated on a continous basis for 28 days to promote the growth of microorganisms in the column. During this time, the tower was seeded with some old blowdown samples which contained visible biological growth. Following this acclimation period a small amount of biomass was visible on the packing at points near the wall of the tower and the final test, L-12 was conducted.

Test operating conditions and blowdown recoveries are given in Table 20. The experimental plan involved three specific liquid/gas ratios, 0.81, 1.6, and 2.4. At each of these L/G ratios, at least three data points at different cycles of concentration were obtained. Makeup rates were adjusted as needed to compensate for changes in ambient air conditions.

## 5.2 Blowdown Recoveries: Results and Discussion

The most consistent result observed was the association between the recovery of phenol in the blowdown and the cycles of concentration (i.e., the recovery of water in the blowdown). These data for the first ten tests (conducted without additives and in the non-bioactive mode) are plotted in Figure 6. The slope of this line is approximately 0.71, which suggests that phenol is about 1.4 times as volatile as water in the system.

## TABLE 20. OPERATING CONDITIONS FOR TESTS IN THE THIRTY CENTIMETER SQUARE COOLING TOWER

| Test | L1 | L2 | L3 | L4 | L5 | L6 | L7 | L8 | L9 | L10 | L11* | L12** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperatures °F | | | | | | | | | | | | |
| Gas In | 22 | 23 | 21 | 22 | 22 | 21 | 21 | 21 | 73 | 21 | 26 | 21 |
| Gas In (wet bulb) | 21 | 21 | 20 | 21 | 21 | 18 | 18 | 18 | 22 | 18 | 24 | 18 |
| Water above nozzle | 51 | 51 | 43 | 43 | 43 | 51 | 52 | 52 | 52 | 52 | 51 | 50 |
| Spray above packing | 48 | 49 | 41 | 42 | 42 | 50 | 50 | 51 | 50 | 51 | 49 | 49 |
| One Foot Down | 48 | 48 | 34 | 35 | 35 | 50 | 50 | 49 | 49 | 50 | 48 | 47 |
| Two Feet Down | 41 | 41 | 33 | 33 | 33 | 47 | 47 | 47 | 44 | 45 | 43 | 43 |
| Sump | 38 | 38 | 31 | 31 | 31 | 40 | 40 | 39 | 39 | 40 | 39 | 37 |
| Liquid/Gas g/g | 1.6 | 1.6 | 0.81 | 0.81 | 0.81 | 2.4 | 2.4 | 2.4 | 1.6 | 1.6 | 1.6 | 1.6 |
| Cycles of Concentration | 15. | 6.0 | 5.4 | 17. | 7.9 | 3.7 | 22. | 4.5 | 5.1 | 8.1 | 19. | 7.9 |
| Circulation Rate mL/sec $cm^2$ | 0.075 | 0.075 | 0.075 | 0.075 | 0.075 | 0.075 | 0.075 | 0.075 | 0.075 | 0.075 | 0.075 | 0.075 |
| Makeup Rate g/min | 83. | 98. | 106. | 83. | 98. | 98. | 73. | 91. | 106. | 91. | 73. | 91. |
| Recoveries in Blowdown (wt. %) | | | | | | | | | | | | |
| Water | 6.7 | 17. | 19. | 5.9 | 13. | 27. | 4.5 | 22. | 20. | 12. | 5.3 | 13. |
| Phenol | 6.9 | 21. | 16. | 3.7 | 6.2 | 17. | 2.6 | 13. | 17. | 7.2 | 4.9 | 12. |
| Hydantoin | 24. | 41. | 31. | 2.4 | 14. | 41. | 14. | 89. | 63. | 38. | 11. | 65. |
| Methanol | 0.4 | 1.1 | 1.3 | 0.3 | 0.8 | 2.4 | 1.1 | 1.9 | 1.2 | 0.7 | 0.2 | 0.7 |
| Acetone | 0.0 | 0.0 | 0.0 | 0.6 | 0.0 | 0.0 | 0.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Acetonitrile | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 11. | 2.7 | 0.0 | NA | NA | NA | NA |
| Ammonia | 5.4 | 2.6 | NA | NA | NA | NA | NA | NA | NA | NA | 1.7 | 7.9 |
| Cyanide | 0.6 | 0.3 | NA | NA | NA | NA | NA | NA | NA | NA | 0.5 | 0.5 |
| Thiocyanate | 37. | 6.8 | 46. | 20. | 51. | 57. | 12. | 59. | 49. | 34. | NA | NA |

*Additives in Makeup
**Bioactivity promoted
NA = not analyzed

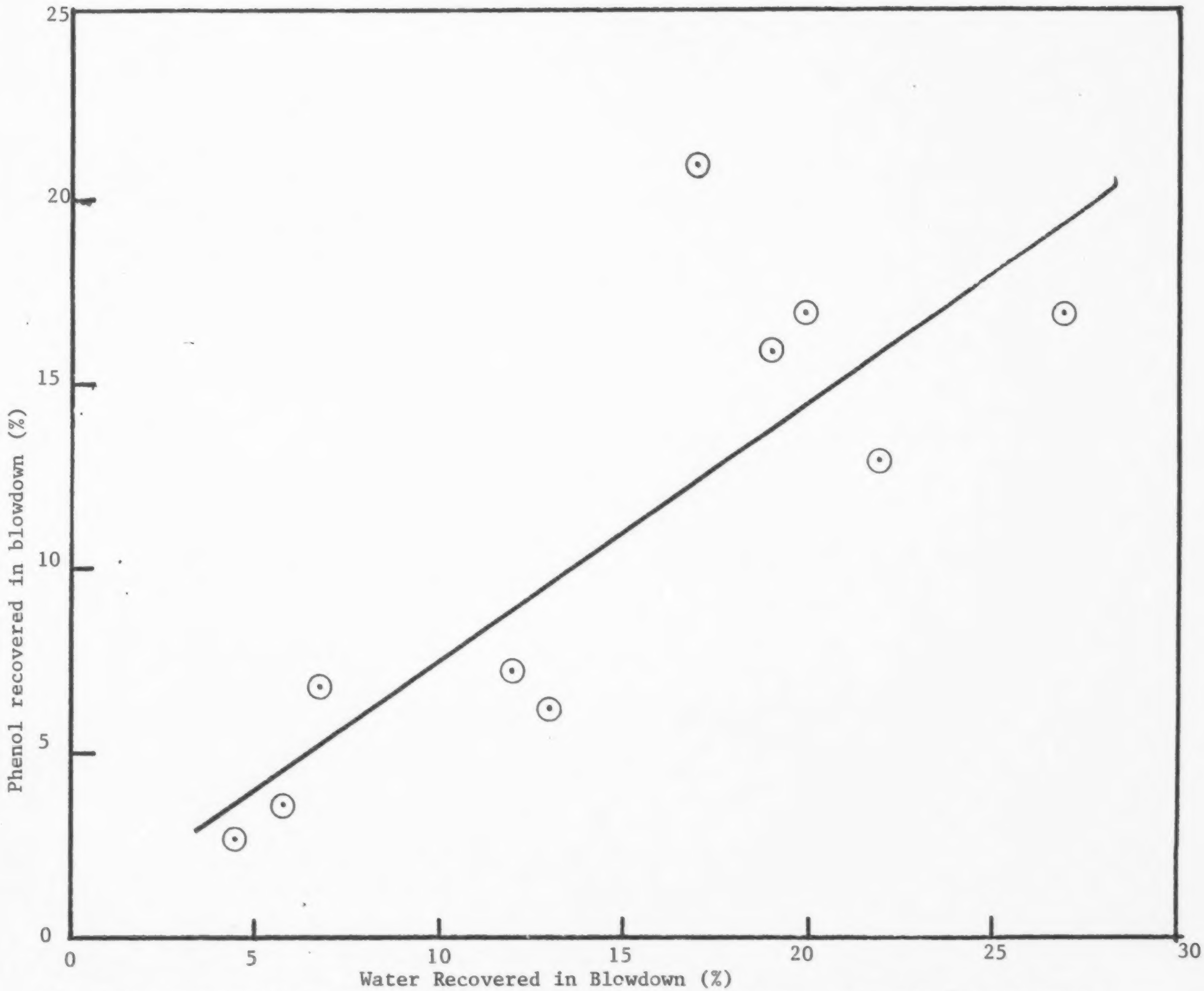

Figure 6. Volatility of phenol relative to water in one foot square cooling tower tests

The components acetone and acetonitrile are much more volatile having relative volatilities 25 and 11 times higher than phenol respectively based on Table 5. Since they were introduced at much lower concentrations than phenol, the concentrations of these components in the blowdown were often below the detection limit of the chemical analysis method used. A comparison of observed relative volatility to predicted relative volatility cannot be made for these components.

Blowdown recoveries of hydantoin were inconsistent. No vapor pressure or activity data are available in the literature for this compound. Based on its high melting point it is expected to be extremely nonvolatile. Thus the incomplete recoveries may be due to a chemical reaction taking place in the cooling tower. This is uncertain however, as the chemical analysis procedure for hydantoin was found to be imprecise and replicate analyses varied within ± 25% of the mean for three analyses. Willson, et al., (1983) found almost 100% recovery of hydantoin derivatives in cooling tower blowdown at 10 cycles of concentration. Comparable data obtained in the 30 cm square laboratory cooling tower ranged from 14 to 65% in tests conducted at 7.9 to 15 cycles of concentration.

A minimum of 97.6% of the methanol present in the makeup water was removed in the cooling tower operation. This minimum was observed for test L-6 which was conducted at the lowest cycles of concentration. The relative volatility of methanol is approximately five times that of phenol.

## 5.3 Vapor Phase Composition

Acid, base, and water impingers were used to obtain vapor phase samples at the top of the cooling tower. Analyses of basic impinger solutions to quantitate phenol concentrations in the vapor yielded unreasonably high values, i.e., 375-2000% of the influent phenol was accounted for. This error may be due to interferences caused by the basic impinger solution, or to a difference in chromatographic response factor caused by the basic nature of the sample. In any case, these data are not reliable. The methanol concentration of the vapor phase was determined relatively accurately as indicated by the mass balances for methanol given in Table 21. These data confirm that nearly all of the methanol introduced in the makeup was stripped in the laboratory tests.

Similar data for ammonia and cyanide were obtained through analysis of acidic and basic impinger solutions. These data are given in Table 22. Both gases were rapidly stripped from solution; the cyanide was almost completely removed (>99%) in the four tests for which data are available.

## 5.4 Cooling Tower Additive Testing

Test L-11 was conducted with the same basic feed composition as the other tests. In addition, cooling tower additives were present in the water for this test in an attempt to determine whether this would affect stripping rates. Calgon CL-37 antifoam and sodium metaphosphate were added at 10 mg/L each and potassium dichromate was added at a concentration of 28 mg/L. The test was conducted under similar conditions to test L-1, but the cycles of concentration were slightly higher, 19 versus 15. Differences in blowdown recoveries of phenol, methanol, acetone, and cyanide between the two tests were minimal. Less hydantoin and ammonia were recovered in the blowdown of test L-11, however, this is probably within the range of experimental variation. In any case, no chemical mechanisms are apparent which would explain this. The pH of the feed solution was approximately 7 and did not change with the addition of the potassium dichromate.

## 5.5 Biological Testing

After a period of biological acclimation, test L-12 was conducted. The same basic feed as that used in tests L-1 through L-10 was used; in addition, 100 mg/L of phosphorus was added as a nutrient. This test was conducted under similar conditions to test L-9, but the cycles of concentration were slightly higher, 7.9 versus 5.1. Blowdown recoveries of phenol, methanol, hydantoin, and acetone were roughly comparable. Blowdown recovery of ammonia was higher in test L-12 but this was not accountable to biological oxidation as the opposite effect would be expected. Here again, variations in blowdown recoveries between the biologically active test (L-12) and the previous tests do not fall outside the range of experimental variation. Following this test the cooling tower sump was sampled and found to contain a total microbial population of 2440/ml. This is not a particularly high concentration for cooling water but presumably most biological oxidation would occur on packing surfaces by fixed film organisms rather than in the cooling tower sump by suspended growth organisms.

TABLE 21. FATE OF METHANOL IN THIRTY CENTIMETER SQUARE COOLING TOWER

| Test | IN Makeup mg/min | OUT Blowdown mg/min | Vapor mg/min | FRACTION ACCONTED FOR % |
|---|---|---|---|---|
| L-1 | 20.6 | 0.1 | 20.6 | 100 |
| L-2 | 24.2 | 0.3 | 18.6 | 78 |
| L-6 | 27.2 | 0.7 | 33.4 | 125 |

## TABLE 22. FATE OF AMMONIA AND CYANIDE IN THE THIRTY CENTIMETER SQUARE LABORATORY COOLING TOWER

| Test | Ammonia | | | | Cyanide | | | |
|---|---|---|---|---|---|---|---|---|
| | IN | OUT | | Accounted for | IN | OUT | | Accounted for |
| | Makeup mg/min | Blowdown mg/min | Vapor mg/min | % | Makeup mg/min | Blowdown mg/min | Vapor mg/min | % |
| 1 | 39 | 2.1 | 75 | 198 | 1.5 | .009 | 2.1 | 139 |
| 2 | 46 | 1.2 | 75 | 166 | 1.7 | .005 | 4.8 | 280 |
| 11 | 34 | 0.57 | 55 | 163 | 1.8 | .009 | NA | NA |
| 12 | 44 | 3.5 | 43 | 106 | 2.4 | .012 | NA | NA |

NA = not analyzed

A drift sample was taken in test L-12 to provide data with regard to the potential dispersal of pathogenic organisms, if such organisms were present in the cooling tower. To promote the formation of drift so as to obtain a sufficient quantity for analysis, the mist eliminator was removed for this test. A beaker was suspended near the top of the tower and a small volume of drift was collected. The top of the beaker was approximately level with the top of the tower and the cross sectional area was small enough so the flow of gases from the top of the tower was not disturbed. The drift sample collected was found to contain 300 organisms/mL. This was only about one-eighth of the population in the sample withdrawn from the sump. Even though the high temperatures near the top of the tower would inhibit bacterial growth, the organism recirculated from the tower sump would be expected to survive the elevated temperatures. In any case, it is likely that organisms present in cooling tower circulating water will be dispersed as drift from the top of the tower.

### 5.6 Application of the Mathematical Model to the Thirty Centimeter Square Cooling Tower

The mathematical model was applied to the thirty centimeter square cooling tower. Sample output for prediction of the fate of phenol at ten cycles of concentration under bioactive conditions is given in Table 23. Predictions of the fate of phenol, methanol, and acetone at varying cycles of concentration under sterile and bioactive conditions are given in Tables 24-26. Experimental data for phenol emissions are shown in Figure 7 along with model predictions. Under sterile conditions, mathematical model predictions of the fate of phenol and acetone closely approximated laboratory data. The model predictions of the fate of methanol overstated the degree of stripping observed in the laboratory to a small extent, but in general essentially complete stripping of methanol under non-bioactive conditions was predicted and observed.

Sensitivity of phenol emissions to changes in operating conditions are given in Table 27. Model predictions indicate that changing operating conditions can have a significant effect on phenol emissions but that over a wide range of tower operating conditions, at least two thirds of the phenol present in the makeup water will be emitted through stripping and drift.

### TABLE 23. MODEL OUTPUT: THE FATE OF PHENOL IN THE THIRTY CENTIMETER SQUARE LABORATORY COOLING TOWER UNDER BIOACTIVE CONDITIONS

---

```
Liquid streams
    Makeup
        Flow rate:      11.7        lb/(sq ft hr)
                        11.7        lb/hr
        Pollutant conc:      160.  ppm
    Circulation
        Flow rate:      550.        lb/(sq ft hr)
                        550.        lb/hr
        Inlet of cooling tower
            Pollutant conc:     87.7 mg/L
            Biomass conc:      322.  mg/L
            Temperature:       124.00 F
        Outlet of cooling tower
            Pollutant conc:     86.2 mg/L
            Biomass conc:      328.  mg/L
            Temperature:       103.11 F
            Oxygen conc:          6.60 ppm
        Heat duty:      0.1149E+05 Btu/hr
        Oxygen conc at holding basin outlet:     6.42 ppm
    Drift
        Flowrate:       0.550E-01lb/(sq ft hr)
                        0.550E-01 lb/hr
        Pollutant conc:      87.7 ppm
        Pollutant emission: 0.482E-05 lb/hr
                            0.412E-06 lb/lb makeup
        Biomass conc:       322.  ppm
        Biomass emission:    0.177E-04 lb/hr
                            0.151E-05 lb/lb makeup
    Blowdown
        Flowrate:       1.11        lb/(sq ft hr)
                        1.11        lb/hr
        Pollutant conc:      87.7 ppm
        Pollutant blowdown:  0.978E-04 lb/hr
                             0.836E-05 lb/lb makeup
        Biomass conc:       322.  ppm
        Biomass blowdown:    0.358E-03 lb/hr
                             0.306E-04 lb/lb makeup
 Gas Stream
     Flow rate:      344. lb/(sq ft hr)
                     344. lb/hr
     Pollutant conc:     1.05 ppmv
     Pollutant emission: 0.125E-02 lb/hr
                         0.107E-03 lb/lb makeup
 Emissions Summary
     % of pollutant report to blowdown:                5.22
     % of pollutant stripped:                         67.01
     % of pollutant evolved with drift:                0.26
     Total % of pollutant emitted to atmosphere:      67.27
     % Pollutant biooxidized:                         27.51
     % Pollutant biooxidized in tower:                27.07
     Emissions of bioactive material:            0.9449E-02
     (lb/lb. pollutant in makeup)
```

TABLE 24. MODEL PREDICTIONS OF THE FATE OF PHENOL IN THE THIRTY CENTIMETER SQUARE LABORATORY COOLING TOWER

| Cycles of Concentration | Removal Mechanism (%)<br>Blowdown | Stripping | Drift | Biological Oxidation |
|---|---|---|---|---|
| | | Bioactive | | |
| 5 | 11.4 | 63.3 | 0.24 | 25.1 |
| 10 | 5.22 | 67.0 | 0.26 | 27.5 |
| 15 | 3.31 | 68.0 | 0.26 | 28.5 |
| 25 | 1.84 | 68.4 | 0.26 | 29.5 |
| | | Sterile | | |
| 5 | 15.2 | 84.5 | 0.32 | ---- |
| 10 | 7.18 | 92.5 | 0.35 | ---- |
| 15 | 4.61 | 95.0 | 0.36 | ---- |
| 25 | 2.59 | 97.0 | 0.37 | ---- |

TABLE 25. MODEL PREDICTIONS OF THE FATE OF METHANOL IN THE THIRTY CENTIMETER SQUARE LABORATORY COOLING TOWER

| Cycles of Concentration | Removal Mechanism (%)<br>Blowdown | <br>Stripping | <br>Drift | <br>Biological Oxidation |
|---|---|---|---|---|
| | | | Bioactive | |
| 5 | 4.06 | 83.6 | 0.09 | 12.2 |
| 10 | 1.79 | 85.4 | 0.09 | 12.8 |
| 15 | 1.13 | 85.8 | 0.09 | 13.0 |
| 25 | 0.62 | 86.1 | 0.09 | 13.2 |
| | | | Sterile | |
| 5 | 4.60 | 95.3 | 0.10 | ---- |
| 10 | 2.04 | 97.8 | 0.10 | ---- |
| 15 | 1.29 | 98.6 | 0.10 | ---- |
| 25 | 0.71 | 99.2 | 0.10 | ---- |

TABLE 26. MODEL PREDICTIONS OF THE FATE OF ACETONE IN THE THIRTY CENTIMETER SQUARE LABORATORY COOLING TOWER

| Cycles of Concentration | Removal Mechanism (%) |  |  |  |
|---|---|---|---|---|
|  | Blowdown | Stripping | Drift | Biological Oxidation |
|  |  |  | Bioactive |  |
| 5 | 1.16 | 95.2 | .02 | 3.62 |
| 10 | 0.50 | 95.8 | .02 | 3.65 |
| 15 | 0.32 | 96.0 | .02 | 3.66 |
|  |  |  | Sterile |  |
| 5 | 1.19 | 98.8 | .03 | ---- |
| 10 | 0.52 | 99.5 | .03 | ---- |
| 15 | 0.32 | 99.7 | .03 | ---- |
| 25 | 0.19 | 99.8 | .03 | ---- |

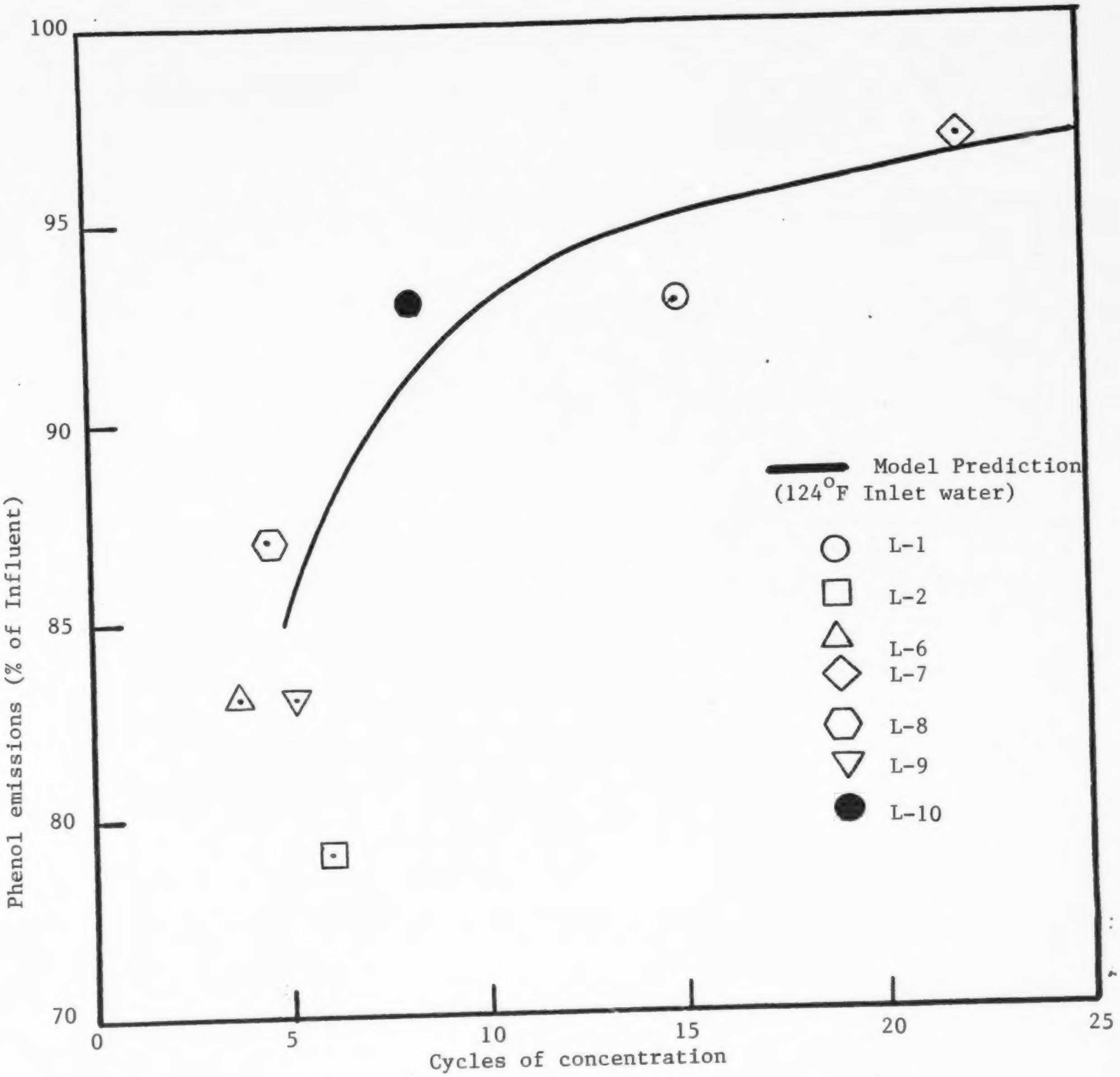

Figure 7. Predicted and observed phenol emissions from the thirty centimeter square laboratory cooling tower assuming sterile conditions.

### TABLE 27. SENSITIVITY OF PHENOL EMISSIONS (STRIPPING AND DRIFT) TO CHANGES IN OPERATING CONDITIONS: THIRTY CENTIMETER SQUARE LABORATORY COOLING TOWER AT TEN CYCLES OF CONCENTRATION UNDER BIOACTIVE CONDITIONS

| | % Emitted |
|---|---|
| Base Case | 67.3 |
| Double Circulation Rate to 9.0 $mL/cm^2$ min | 77.3 |
| Raise Inlet Liquid Temperature to 60°C | 73.4 |
| Double Phenol Concentration in Makeup to 320 mg/L | 73.4 |

# 6.0 APPLICATION OF THE COOLING TOWER MATHEMATICAL MODEL TO THE UNDERC COOLING TOWER

The cooling tower mathematical model has been applied to the experimental cooling tower operated by the University of North Dakota Energy Research Center (UNDERC), described by Willson, et al., (1983). The UNDERC cooling tower is a forced draft counter-current flow tower with corrugated PVC packing. For the tests described by Willson, et al., (1973) a packing cross-sectional area of 4600 $cm^2$ was used; the packing height was 200 cm. The test was conducted with extracted, stripped gas liquor from the UNDERC gasifier. The tower was operated to achieve approximately ten cycles of concentration on a twenty-four hour average basis.

The mathematical model was used with input parameters reported for the UNDERC cooling tower, to predict the fate of phenol in the system. Input data are given in Table 28. Sample model output is given in Table 29. A comparison of model predictions of dependent variables with observed values of these variables is given in Table 30. The model predictions are reasonable, particularly the predictions of phenol emission through air stripping and drift.

The sensitivity of the prediction of phenol emissions to variations in the UNDERC cooling tower operating conditions was determined by varying the base case model parameters. Results are given in Table 31. Consistent with the results of the RTI laboratory tests, tower operating conditions, other than cycles of concentration, do not have a major impact on the proportion of phenol in the column feed emitted to the atmosphere through air stripping. It should be noted that a doubling of phenol concentration in the tower makeup does result in an approximate doubling of mass emissions of phenol.

The effect of cycles of concentration on emissions in the absence of biooxidation is shown in Figure 8. At the base case (see Table 28) operating conditions a family of curves is shown for components with varying relative (to water) volatilities. The curve with relative volatility equal to one shows the emission of water from the tower. It should be noted that the curve does not show a perfect inverse relationship between emissions and cycles of concentration for water due to the

TABLE 28. MODEL PARAMETERS FOR UNDERC COOLING TOWER

ZLZ - circulation rate: 900 lb/ft$^2$ hr = 7.3 mL/cm$^2$ min

TL - inlet water temperature: 120°F = 49°C

GP - gas flow rate: 872 lb dry air/ft$^2$ hr = 7.1 g/cm$^2$ min

XHO - inlet gas enthalpy: 26.4 Btu/lb dry air = 14.7 cal/g

YO - inlet gas humidity: 0.00886 lb $H_2O$/lb dry air = 0.00886 g $H_2O$/g dry air

PDRIF - drift rate: 0.05 percent of circulation rate

PT - atmospheric pressure: 14.7 psia = 1.0 atm

- column characteristics
    - Z - packing height: 1.5 ft = 46 cm
    - ZM - Merkel number : 2.25
    - CAREA - Cross sectional area: 5 ft$^2$ = 4600 cm$^2$
    - FL - liquid holdup: 0.05 ft$^3$ liquid/ft$^3$ packing = 0.05 cm$^3$/cm$^3$
    - SAREA - specific surface area: 40 ft$^2$/ft$^3$ = 1.3 cm$^2$/cm$^3$

VH - Holding basin volume: 26.7 ft$^3$ = 756 L

CC - cycles of concentration: 10

- pollutant characteristics (Phenol)
    - AS,BS - TP$_{vap}$(psia) = exp(18.084-9916.9/(T+460°F))
    - SMW - molecular weight: 94
    - CS - makeup concentration: 150 mg/L
- biokinetics
    - Michaelis - Menton
        - AKO - k = 1.0 g BOD/(g biomass day)
        - AKS - $k_s$ = 266 mg BOD/liter
        - AKD - $K_d$ = 0.033 day$^{-1}$
        - Y - Y = 0.37 g biomass/g BOD

          monolayer constant
        - AKT - $k_t$ = 1.33 x $10^{-4}$ g biomass/cm$^2$ of packing

## TABLE 29. MODEL OUTPUT FOR UNDERC COOLING TOWER

```
Liquid streams
     Makeup
          Flow rate:            36.2 lb/(sq ft hr)
                               181.  lb/hr
          Pollutant conc:            150. ppm
     Circulation
          Flow rate:           900.  lb/(sq ft hr)
                                 0.450E+04 lb/hr
          Inlet of cooling tower
               Pollutant conc:      96.0 ppm
               Biomass conc:        79.8 ppm
               Temperature:       120.00 F
          Outlet of cooling tower
               Pollutant conc:      94.0 ppm
               Biomass conc:        83.0 ppm
               Temperature:         82.06 F
               Oxygen conc:          7.90 ppm
          Heat duty:     0.1707E+06 Btu/hr
          Oxygen conc at holding basin outlet:    6.96 ppm
     Drift
          Flowrate:      0.450      lb/(sq ft hr)
                         2.25       lb/hr
          Pollutant conc:      96.0 ppm
          Pollutant emission:  0.216E-03 lb/hr
                               0.119E-05 lb/lb makeup
          Biomass conc:        79.8 ppm
          Biomass emission:    0.180E-03 lb/hr
                               0.992E-06 lb/lb makeup
     Blowdown
          Flowrate:      3.17       lb/(sq ft hr)
                        15.9        lb/hr
          Pollutant conc:      96.0 ppm
          Pollutant blowdown:  0.152E-02 lb/hr
                               0.841E-05 lb/lb makeup
          Biomass conc:        79.8 ppm
          Biomass blowdown:    0.127E-02 lb/hr
                               0.699E-05 lb/lb makeup
Gas Stream
     Flow rate:     872.      lb/(sq ft hr)
                      0.436E+04 lb/hr
     Pollutant conc:     1.54 ppmv
     Pollutant emission: 0.235E-01 lb/hr
                         0.129E-03 lb/lb makeup
Emissions Summary
     % of pollutant report to blowdown:                   5.61
     % pollutant stripped:                               86.32
     % pollutant evolved with drift:                      0.80
     Total % of pollutant emitted to atmosphere:         87.12
     % pollutant biooxidized:                             7.28
     % pollutant biooxidized in tower:                    2.92
     Emissions of bioactive material:         0.6612E-02
     (lb/lb pollutant in makeup)
```

TABLE 30. PREDICTION OF UNDERC COOLING TOWER PERFORMANCE

| | Computed | | Observed |
|---|---|---|---|
| | Sterile | Bioactive | |
| Blowdown rate, L/hr | 7.20 | 7.20 | 6.12 |
| Phenol recovered in blowdown, % | 6.1 | 5.6 | 8.7 |
| Makeup rate, L/hr | 82.0 | 82.0 | 63.4 |
| Phenol emitted to atmosphere, % | 94 | 87 | 91. |

## TABLE 31. EFFECT OF VARIATIONS TO BASE CASE OPERATING CONDITIONS OF PHENOL EMISSIONS FROM THE UNDERC COOLING TOWER

| | % Phenol emitted to atmosphere |
|---|---|
| Base case (See Table 28) | 87(94)* |
| Liquid circulation rate increased from 7.3 to 8.5 mL/$cm^2$ min | 89 |
| Inlet liquid temperature increased from 49 to 60°C | 89 |
| Makeup phenol concentration increased from 150 to 300 mg/L | 82(94)* |
| Merkel number and packing height doubled | 86 |

* no biooxidation

effect of drift. Thus, for a relative volatility of one (i.e., equal to that of water) and 10 cycles of concentration, slightly more than 90% of the makeup is emitted to the atmosphere.

Figure 9 shows similar outputs for components with biochemical oxidation based on kinetics reported by Hicks, et al. (1979). In this case it is seen that high cycles of concentration result in decreased emissions and increased biological oxidation. The general explanation for this is that at higher cycles of concentration the steady-state pollutant concentration in the tower is lower resulting in lower rates of air stripping relative to biological oxidation.

Mathematical model predictions of the fate of methanol, acetone, and acetonitrile in the UNDERC cooling tower were made based on vapor pressure data given in Section 3. Predictions for acetonitrile in the absence of bioactivity are given in Table 32. Calculations for acetone have been made with and without bioactivity. These results are shown in Table 33. Stripping of this component is so rapid as to make biological oxidation negligible. Comparable results for methanol are given in Table 34, where, on the assumption that methanol is of equal biodegradability as phenol, biological oxidation is seen to account for approximately 1% of methanol removed at very high cycles of concentration. The effect of cycles of concentration on methanol stripping under UNDERC cooling tower conditions is shown in Figure 10.

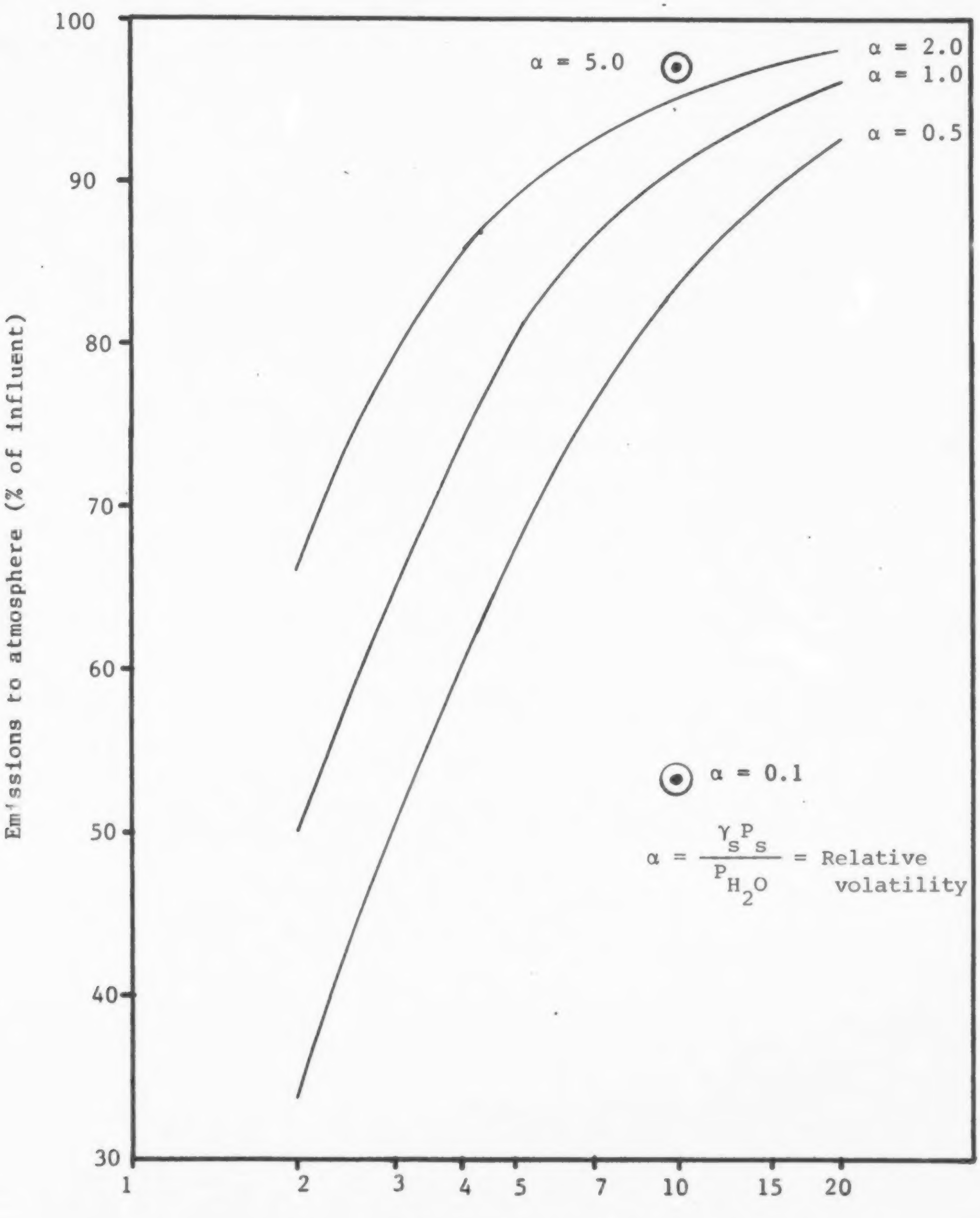

Figure 8. Emissions to atmosphere under UNDERC base case conditions with no bio-oxidation.

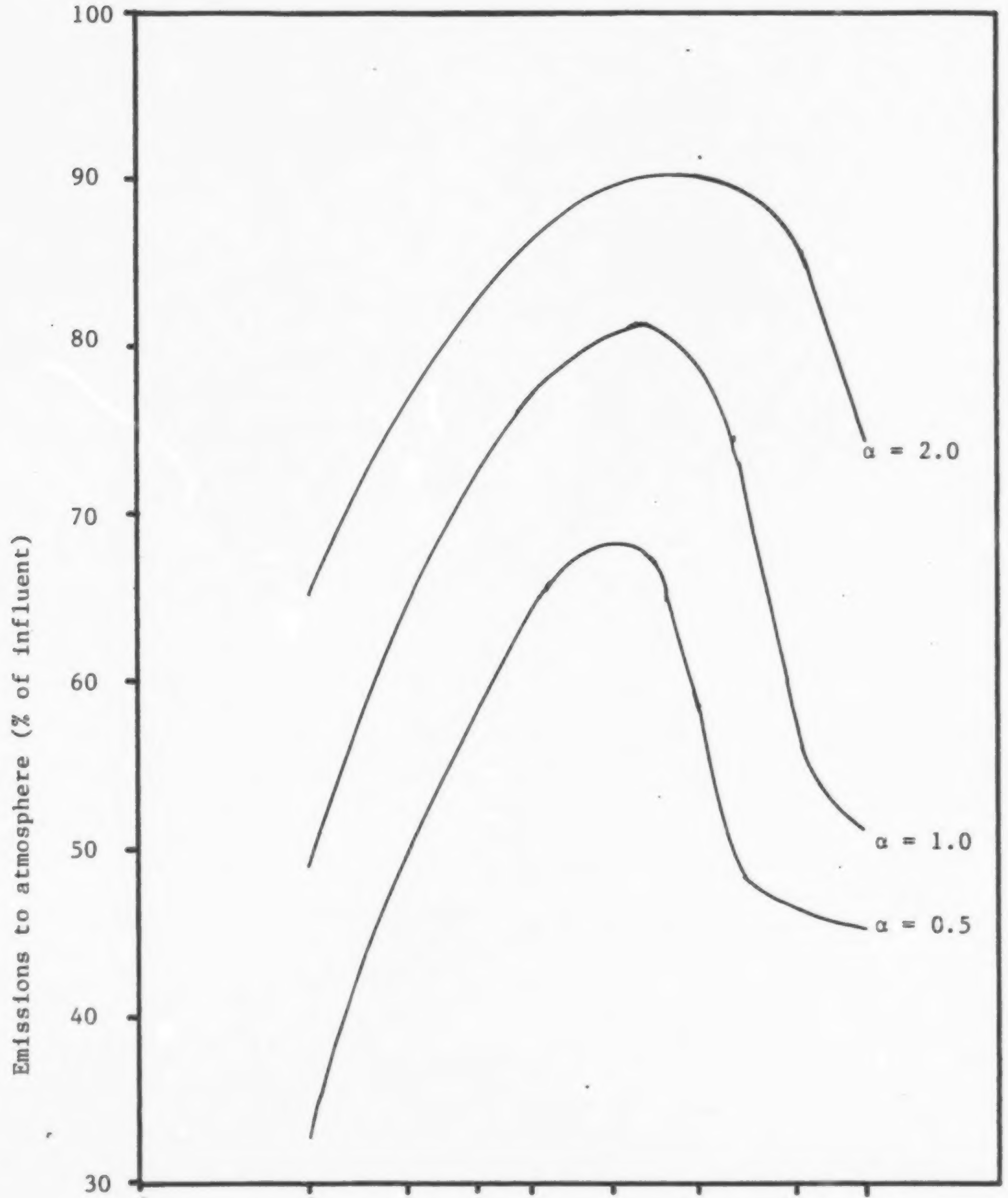

Figure 9. Emissions to atmosphere under UNDERC base case conditions for pollutants with biokinetic rates from Hicks et al., (1979).

TABLE 32. MODEL PREDICTIONS OF THE FATE OF ACETONITRILE IN THE UNDERC COOLING TOWER UNDER NON-BIOACTIVE CONDITIONS (Makeup Concentration - 2 mg/L)

| Mechanism | Cycles of Concentration | | |
|---|---|---|---|
| | 5 | 10 | 15 |
| | % Removed | | |
| Stripping | 98.44 | 99.30 | 99.66 |
| Blowdown | 1.46 | 0.60 | 0.23 |
| Drift | 0.10 | 0.10 | 0.10 |

TABLE 33. MODEL PREDICTIONS OF THE FATE OF ACETONE IN THE UNDERC COOLING TOWER (Makeup Concentration = 10 mg/L)

| Mechanism | Cycles of Concentration and bioactivity | | |
|---|---|---|---|
| | 5, bioactive | 5, sterile | 10, sterile |
| | % Removed | | |
| Stripping | 99.12 | 99.12 | 99.61 |
| Blowdown | 0.82 | 0.82 | 0.33 |
| Drift | 0.06 | 0.06 | 0.06 |
| Biooxidation | 0.00 | ---- | ---- |

--- Not applicable

TABLE 34. MODEL PREDICTIONS OF THE FATE OF METHANOL IN THE UNDERC COOLING TOWER (Makeup Concentration = 250 mg/L)

| | % Removed | | | |
|---|---|---|---|---|
| | Stripping | Blowdown | Drift | Biooxidation |
| 5 cycles of concentration, bioactive | 96.65 | 2.36 | 0.16 | 0.83 |
| 10 cycles of concentration, bioactive | 97.96 | 0.97 | 0.17 | 0.90 |
| 15 cycles of concentration, bioactive | 98.32 | 0.57 | 0.17 | 0.95 |
| 25 cycles of concentration, bioactive | 98.50 | 0.26 | 0.17 | 1.08 |
| 5 cycles of concentration, sterile | 97.45 | 2.38 | 0.17 | --- |
| 10 cycles of concentration, sterile | 98.85 | 0.98 | 0.17 | --- |
| 20 cycles of concentration, sterile | 99.45 | 0.38 | 0.17 | --- |

--- not applicable

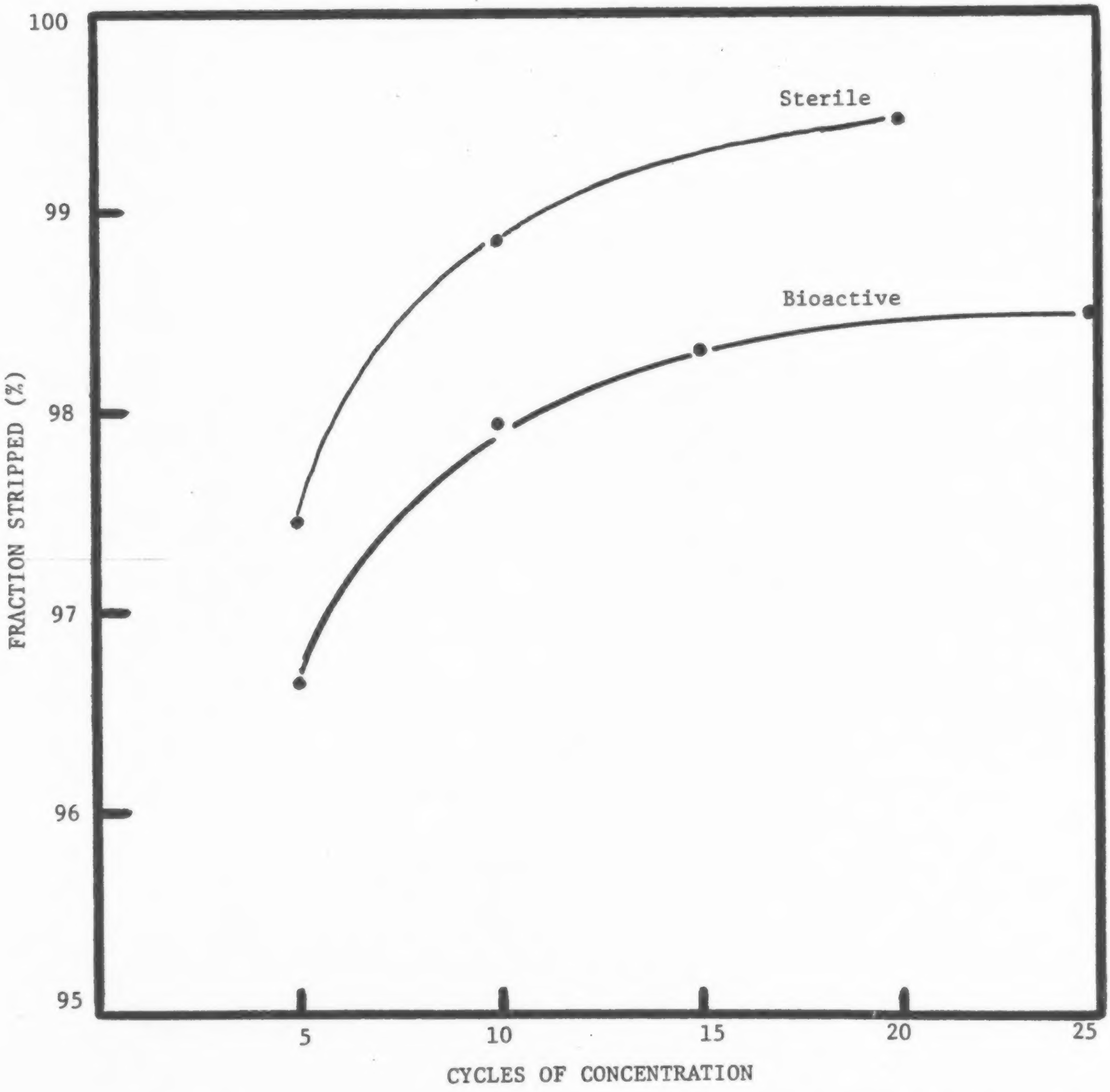

FIGURE 10. Model Prediction of the Effect of Cycles of Concentration on Stripping of Methanol from the UNDERC Cooling Tower (Makeup Concentration = 250 mg/L)

## 7.0 QUALITY CONTROL FOR LABORATORY MEASUREMENTS

In the laboratory experiments involving operation of the five centimeter diameter and 30 centimeter square laboratory cooling towers, physical measurements as well as chemical analyses were obtained. Chemical analyses were directed towards determination of removal rates and mechanisms; physical measurements were made to characterize the process conditions under which these removal mechanisms took place.

### 7.1 Physical Measurements

Physical measurements involved determination of temperatures and gas and liquid flow rates. Objectives for quality control of these measurements in terms of accuracy, completeness and precision were met. All temperatures were measured with type J thermocouples connected to digital readouts. These devices displayed data to the nearest 1°C. As a result, a slight fluctuation in actual temperature, e.g., from 25.4°C to 25.5°C would result in a change of 1°C in readout. This did not adversely affect the quality of the data analysis. Liquid flow measurements were made through volumetric pump calibrations involving integration over a sufficient time interval to keep measured volumetric flow rates within ±1% of actual rates. Factors limiting accuracy in this case were readability of graduations on volumetric glassware. Air flow measurements for the 5 cm tower were made with a wet test meter; specified accuracy for this instrument was ±0.5%. Since this is the type of instrument used for calibration of other gas flow meters, no meter of greater accuracy was available for comparative purposes. Results of energy balance calculations which involve temperature, gas flow and liquid flow data were reasonable and energy balances from preliminary testing pointed out the need for improved insulation of the 5 cm tower. Air flow measurements for the 30 cm tower were made with a electronic anemometer having specified accuracy of ±1% for a point measurement. Aside from confirming the zero of the instrument, this could not be evaluated as no higher accuracy meter was available to check it against. Completeness for physical measurements was essentially 100%.

## 7.2 Chemical Analyses

Chemical analyses were performed for determination of phenol, hydantoin, methanol, acetonitrile, acetone, ammonia, cyanide, and thiocyanate. Organics were analyzed by gas chromatography. Ammonia was analyzed with a selective ion electrode; thiocyanate and cyanide were analyzed by wet chemical methods. Organic analyses were done in triplicate. Precision, as measured by maximum deviation from the mean of individual analyses was within ±15% of the mean for phenol and methanol. Except near detection level, precision was ±15% for acetone. Precision for hydantoin analyses was ±25%. Precision for acetonitrile is difficult to assess as maximum concentration of 2 mg/L were close to the detection level and blowdown samples were frequently below the detection level. Selected samples were analyzed in duplicate for ammonia, cyanide, and thiocyanate. These duplicates were within ±10% of the mean for cyanide and thiocyanate. For ammonia samples, a high concentration duplicate analysis was within ±5% of the mean and low concentration duplicates were within ±20% of the mean.

For chromatographic analyses, no independent assessment of accuracy was made. On each day that samples were analyzed, a three point linear concentration curve was prepared using serial dilutions of the feed solution as a standard, bracketing the range of interest. These standards incorporated any matrix effects or interferences to be expected in the samples. The standard determinations were also made in triplicate. Systematic biases in chromatographic response are minimized (for the simulated wastewater tests) by the data analysis procedure; data are reported as recoveries (i.e., fraction of component mass in feed retained in blowdown). A shift in chromatographic response which inflated concentration by a constant factor would not affect reported recoveries. Samples obtained during the tests with UNDERC extracted, stripped gas liquor were analyzed against laboratory standards prepared in the same manner as simulated makeup water. Accuracy of cyanide and thiocyanate analyses was within ±5% as determined by analysis of independent standards. Accuracy of reported ammonia analyses was within ±15% as determined by analysis of independent standards. Accuracy of the calculated recoveries are expected to be better than those for individual analyses due to the cancellation of some of the systematic errors. Original quality control objectives for accuracy were not met, however, the accuracy which was achieved is adequate to draw valid conclusions with regard to the fate of contaminants (of the type measured) if present in cooling tower makeup water. A comparison of the precision achieved to that of the QA objectives is given in Table 35.

With respect to blowdown recoveries, completeness of analyses were phenol (97%), hydantoin (90%), methanol (100%), acetone (100%), acetonitrile (68%), ammonia (52%), cyanide (32%), and thiocyanate (52%). Completeness of vapor phase analyses were phenol (3%), methanol (19%), ammonia (19%), and cyanide (13%). No vapor phase samples were reliably analyzed for hydantoin, acetone, acetonitrile, or thiocyanate due to inadequacies in the sampling methods used. No drift samples were analyzed because neither the 5 cm diameter tower nor the 30 cm square tower generated measureable quantities of drift as operated. It was originally planned to analyze all blowdown samples from the 30 cm square tower for chloride so that cycles of concentration could be calculated on the basis of chloride balance as well as water balance. Considerable effort was expended on these analyses but measured concentrations for makeup solutions were consistently biased several hundred percent high. This was attributed to interference with an undetermined component of the makeup water because independent sodium chloride/water samples were analyzed with acceptable accuracy.

## 7.3 Significant Problems Encountered

Vapor phase sampling with the condensor/cold trap system originally designed was unreliable because the cold trap inlet became progressively more restricted as moisture froze on its walls, resulting in an inconsistent flow split to the trap. In addition, the trap eventually plugged which limited the sampling period. Only qualitative data could be obtained with this system. The resulting failure to close mass balances necessitated greater reliance on assumptions. This system was replaced with acidic and basic impingers which were much more effective in capturing methanol, ammonia, and cyanide.

The original gas volume measurement procedure for the 30 cm square tower involved measurement of a very low gas velocity in the duct connecting the blower to the tower. Flow measurements were made much more reliable with the installation of a 5 cm tube in this duct. With all gas flow

TABLE 35. PRECISION OF CHEMICAL ANALYSES

| SPECIES | PRECISION OBJECTIVE | (%) ACHIEVED |
|---|---|---|
| phenol | 10 | 15 |
| methanol | 10 | 15 |
| acetone | 10 | 15* |
| hydantoin | 10 | 25 |
| acetonitrite | 10 | ND |
| cyanide | 10 | 10 |
| thyiocyanate | 10 | 10 |
| ammonia | 10 | 20 |

* except near detection limit

ND - not determinable

forced through this tube the much higher velocities could be measured with greater accuracy. This improved accuracy to a level adequate for data analysis.

Progressive decline in the response of the flame ionization detector on the Varian chromatograph led to inspection and complete rebuilding of the detector. This resulted in improved response, signal-to-noise ratio and accuracy.

It was found that a consistent circulation rate could not be maintained in the 5 cm tower with the peristaltic pump originally purchased for this purpose. This was replaced with a positive displacement metering pump. This improved operation so that steady state conditions could be reached.

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# APPENDIX A. COMPUTER PROGRAM

The following computer program is written in FORTRAN and has been run on a Digital Equipment Company VAX/VMS computer system. A logic flowsheet for the program is given in Figure A-1. A schematic diagram of the mass and energy streams in a crossflow cooling tower is given in Figure A-2. Input data is read from a data file created by the user which must be named CT.DAT. The format of CT.DAT is shown in Table A-1. Variables to be specified in CT.DAT are defined in Table A-2. The mass transfer characteristics of the cooling tower are specified as ZM, corresponding to the tower characteristics or Merkel number. For a tower in the design stage, this number can be obtained from correlations provided by the manufacturer of the particuar packing to be used in the tower. For an actual operating tower, this number can be calculated from inlet and outlet water temperature, the air wet bulb temperature and the liquid-to-gas ratio. Using a numerical integration technique described in Perry and Chilton (1973) this number can be calculated as follows:

$$\mathrm{ZM} = \frac{T_1 - T_2}{4} \sum_{i=1}^{4} \frac{1}{h_{wi} - h_{ai}}$$

where $T_1$ = water inlet temperature °F

$T_2$ = water outlet temperature °F

$h_{w1}$ = enthalpy of wet air at $T_2+0.1(T_1-T_2)$, Btu/lb dry air

$h_{w2}$ = enthalpy of wet air at $T_2+0.4(T_1-T_2)$, Btu/lb dry air

$h_{w3}$ = enthalpy of wet air at $T_2+0.6(T_1-T_2)$, Btu/lb dry air

$h_{w4}$ = enthalpy of wet air at $T_2+0.9(T_1-T_2)$, Btu/lb dry air

$h_{a1}$ = $h_{wB} + 0.1\ (L/G)(T_1-T_2)$, Btu/lb dry air

$h_{a2}$ = $h_{wB} + 0.4\ (L/G)(T_1-T_2)$, Btu/lb dry air

$h_{a3}$ = $h_{wB} + 0.6\ (L/G)(T_1-T_2)$, Btu/lb dry air

$h_{a4}$ = $h_{wB} + 0.9\ (L/G)(T_1-T_2)$, Btu/lb dry air

$h_{wB}$ = enthalpy of wet air at ambient air wet bulb temperature, Btu/lb dry air

L/G = liquid-to-gas ratio lb/lb

A table of enthalpy data is given in Appendix B.

Sample output data are given in Table A-3. A program listing follows. This program has also been run with slight modifications on an IBM personal computer equipped with a Microsoft Fortran Compiler. In modifying the program to run on the microcomputer system, four changes were made.

1. The FORMAT specifications for the READ statements were changed to fixed fields and the data file was constructed according to the modified FORMAT specifications.

2. Some of the longer program lines in the SOLVE subroutine were divided into two separate lines of less than 70 characters each.

3. An OPEN statement was added to assign a device number to the input data file.

4. A $DO66 statement was added to specify the DO loop configuration used.

The program as listed can be run on a DEC VAX system without modification. For other installations, modifications similar to those listed above may be required depending on the computer and compiler available.

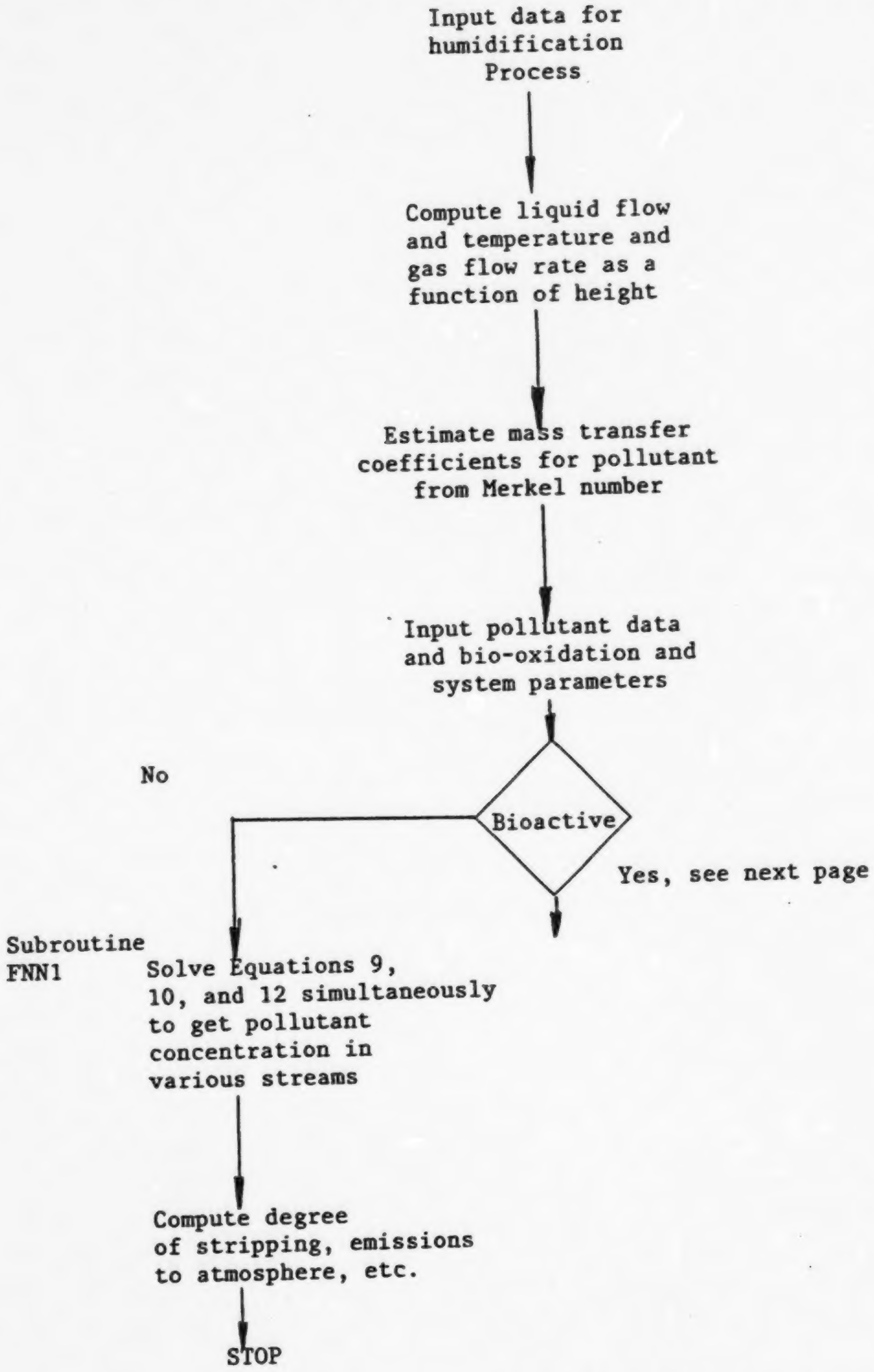
Input data for humidification Process
Compute liquid flow and temperature and gas flow rate as a function of height
Estimate mass transfer coefficients for pollutant from Merkel number
Input pollutant data and bio-oxidation and system parameters
Bioactive
No
Yes, see next page
Subroutine FNN1
Solve Equations 9, 10, and 12 simultaneously to get pollutant concentration in various streams
Compute degree of stripping, emissions to atmosphere, etc.
STOP

Figure A-1. Mathematical Model Flowsheet

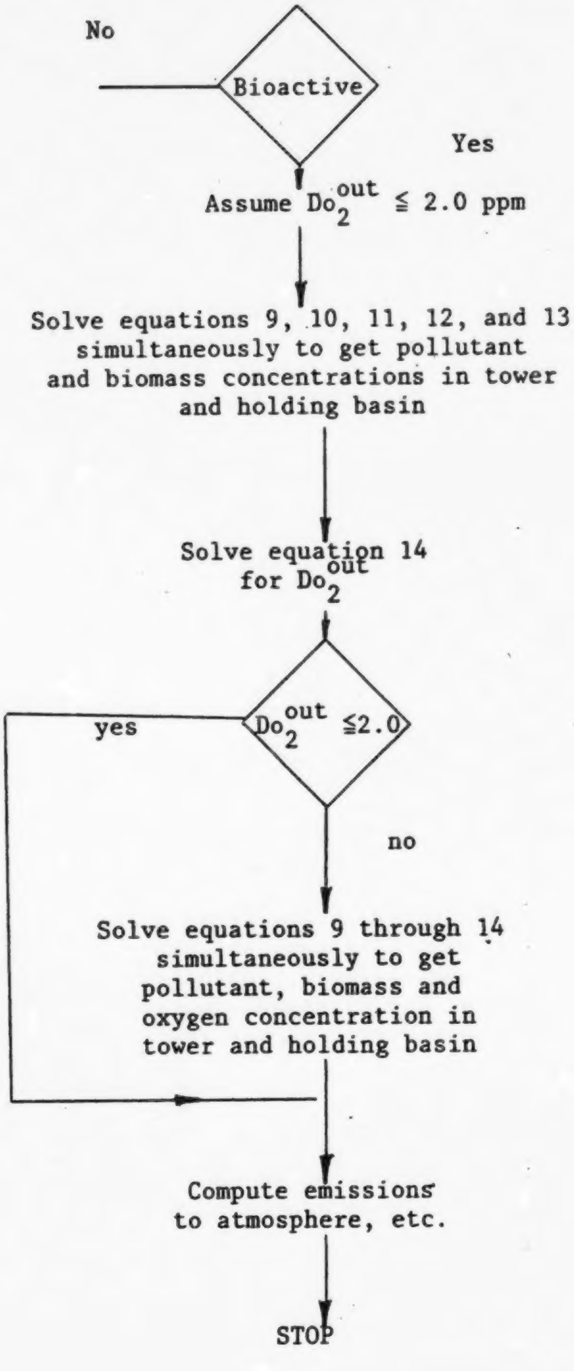
No
Bioactive
Yes
Assume $Do_2^{out} \leqq 2.0$ ppm
Solve equations 9, 10, 11, 12, and 13 simultaneously to get pollutant and biomass concentrations in tower and holding basin
Solve equation 14 for $Do_2^{out}$
yes
$Do_2^{out} \leqq 2.0$
no
Solve equations 9 through 14 simultaneously to get pollutant, biomass and oxygen concentration in tower and holding basin
Compute emissions to atmosphere, etc.
STOP

Figure A-1 (continued). Mathematical Model Flowsheet

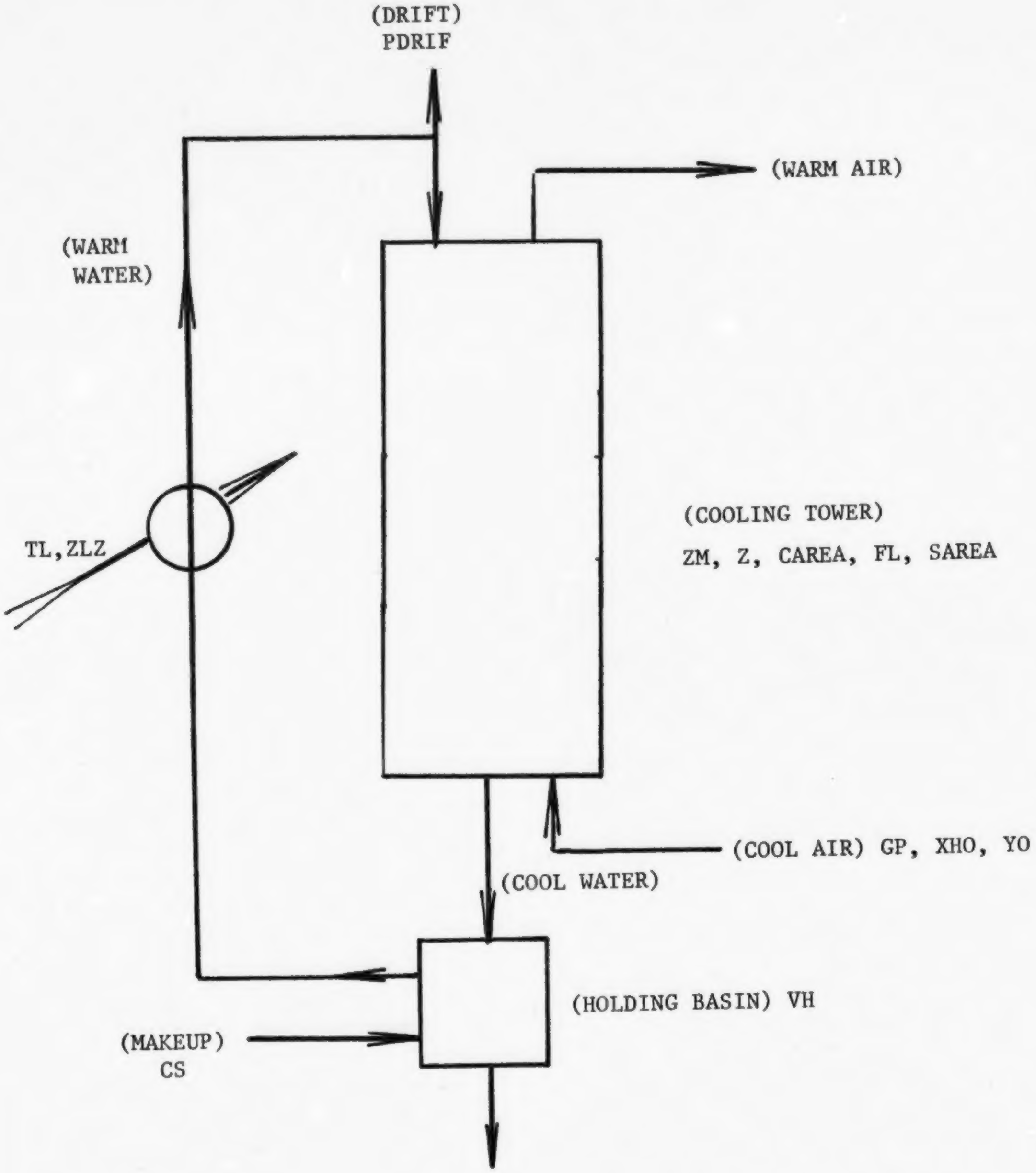
(DRIFT)
PDRIF
(WARM AIR)
(WARM
WATER)
TL,ZLZ
(COOLING TOWER)
ZM, Z, CAREA, FL, SAREA
(COOL AIR) GP, XHO, YO
(COOL WATER)
(HOLDING BASIN) VH
(MAKEUP)
CS

Figure A-2. Cooling Tower Schematic

## TABLE A-1. FORMAT FOR CT.DAT

NBS

PT,ZM,Z,CAREA

FL,SAREA,PDRIF

VH,CC

GP,XHO,YO

TLZ,ZLZ

X1(1), X1(2), ER1, IT1, D

AS, BS, STOICH, CS, SMW

AKO, AKS, AKD, Y, AKT, TREF

X2(1), X2(2), X2(3)

ER2, IT2, D

## TABLE A-2. INPUT DATA FOR CT.DAT

---

NBS = 0 if sterile, 1 if bioactive

PT = Total pressure, psia

ZM = Merkel number

Z = Tower height, ft

CAREA = Cross sectional area of tower, $ft^2$

FL = Liquid hold up $ft^3$ liq/$ft^3$ tower

SAREA = Specific area of packing $ft^2$ surface/$ft^3$ tower

PDRIF = Percent of recirculation that becomes drift

VH = Volume of holding basin, $ft^3$

CC = Cycles of concentration

GP = Gas flow rate, lb dry air/($ft^2$ hr)

XHO = Enthalpy of inlet air, Btu/lb dry air

YO = Humidity, lb $H_2O$/lb dry air

TL = inlet temperature of liquid to tower, °F

ZLZ = Liquid circulation rate, lb/($ft^2$ hr)

X1(1) = Initial estimates of outlet liquid flow rate from tower, lb/($ft^2$ hr) (ZLZ is generally close enough)

X1(2) = Initial estimate of outlet liquid temperature, °F

ER1 = Convergence parameter, use 0.0001

IT1 = Number of iterations, use 50

D = Option parameter, use -1.0

AS specify such that $\gamma_s P_s$ = EXP(AS + BS/T)

BS where $P_s$ = vapor pressure of pollutant, psia

$\gamma_s$ = activity coefficient

and T = temperature °R = °F +460

TABLE A-2. (continued)

STOICH = lb mol $O_2$ needed for biooxidation per lb mole of pollutant

CS = concentration of pollutant makeup, mg/L

SMW = molecular weight of pollutant

AKO = Michaelis-Menton parameter; g BOD/(g biomass)(day)

AKS = Michaelis-Menton parameter; mg BOD/liter

AKD = Michaelis-Menton parameter; $day^{-1}$

Y = Michaelis-Menton parameter; mg biomass/mg BOD

AKT = Monolayer packing constant = 1.333E-4 g

TREF = Reference temperature for Michaelis-Menton parameters, °F

X2(1) = Initial estimate of pollutant concentration in liquid outlet stream of tower, mole fraction

X2(2) = initial estimate of biomass concentration in liquid outlet stream of tower, mg/liter

X2(3) = initial estimate of $O_2$ concentration in liquid outlet stream of holding basin, mg/L

ER(2) = convergence parameter, use 0.00001

IT2 = convergence parameter, use 50

D = convergence parameter, use -1.0

# TABLE A-3. MODEL OUTPUT: FATE OF PHENOL IN THE FIVE CENTIMETER LABORATORY COOLING TOWER AT 10 CYCLES OF CONCENTRATION

---

```
Liquid Streams
    Makeup
        Flow rate:      7.71        lb/(sq ft hr)
                        0.168       lb/hr
        Pollutant Conc:      150. ppm
    Circulation
        Flow Rate:      190.        lb/(sq. ft hr)
                          4.15      lb/hr
        Inlet of cooling tower
            Pollutant conc:      46.7 ppm
            Biomass conc:       492.  ppm
            Temperature:        122.00 F
        Outlet of cooling tower
            Pollutant conc:      42.4 ppm
            Biomass conc:       512.  ppm
            Temperature:         79.42 F
            Oxygen conc:          8.12 ppm
        Heat duty:      176.5       Btu/hr
        Oxygen Conc at holding basin outlet:     7.66 ppm
    Drift
        Flow rate:      0.950E-011b/(sq ft hr)
                        0.207E-02 lb/hr
        Pollutant conc:      46.7 ppm
        Pollutant emission: 0.968E-07 lb/hr
                            0.575E-06 lb/lb makeup

        Biomass conc:       492.  ppm
        Biomass emission:    0.102E-05 lb/hr
                             0.606E-05 lb/lb makeup

     Blowdown
        Flow rate:      0.676       lb/(sq ft hr)
                        0.147E-01 lb/hr
        Pollutant conc:      46.7 ppm
        Pollutant blowdown:  0.689E-06 lb/hr
                             0.409E-05 lb/lb makeup

        Biomass conc:       492.  ppm
        Biomass blowdown:    0.725E-05 lb/hr
                             0.431E-04 lb/lb makeup

  Gas stream
     Flow rate:      157.        lb/(sq ft hr)
                       3.43      lb/hr
     Pollutant conc:      0.962      ppmv
     Pollutant emission: 0.117E-04 lb/hr
                         0.693E-04 lb/lb makeup

  Emissions Summary                                              2.73
      % of pollutant report to blowdown:                        46.19
      % pollutant stripped:                                      0.38
      % pollutant evolved with drift:                           46.57
      Total % of pollutant emitted to atmosphere:               50.70
      % pollutant biooxidized:                                  49.81
      % pollutant biooxidized in tower:
      Emissions of bioactive material:   0.4038E-01
      (lb/lb pollutant in makeup)
```

```
         IMPLICIT DOUBLE PRECISION (A-H,O-Z)
         COMMON PT,XHO,YO,GP,TLZ,ZLZ,ZM,ZL(52),TL(52),
       1 GM(52),DZM,PDRIF,XS(52),XB(52),YS(52),CONS1,
       2 CONS2,FXS,AKO,TREF,DZ,AKYA,AS,BS,FL,SAREA,AKT,
       3 AKS,Y,AKD,CONS3,VH,CAREA,FMAKE,CS,SMW,FBLOW
       4 ,DO2IN,DO2,NBS,NSW
         EXTERNAL FUN1,FUN2
         DIMENSION X1(2),A1(2,2),F1(2),XT1(2),FT1(2),
       1 Y1(4),L1(6),X2(3),A2(3,3),F2(3),XT2(3),
       2 FT2(3),Y2(6),L2(9)
         CALL ASSIGN(1,'CT.DAT')
         CALL ASSIGN(2,'CTO.DAT')
         CALL ASSIGN(5,'TI:')
         READ(1,205)NBS
  205    FORMAT(I5)
         READ(1,105)PT,ZM,Z,CAREA
  105    FORMAT(4G12.5)
         READ(1,106)FL,SAREA,PDRIF
  106    FORMAT(3G12.5)
         READ(1,107)VH,CC
  107    FORMAT(2G12.5)
         READ(1,115)GP,XHO,YO
  115    FORMAT(3G12.5)
         READ(1,125)TLZ,ZLZ
  125    FORMAT(2G12.5)
         READ(1,135)X1(1),X1(2),ER1,IT1,D
  135    FORMAT(3G12.5,I5,G12.5)
         ZM=ZM*ZLZ/GP
         DZM=ZM/50.0
         P=0.0
         CALL SOLVE(2,FUN1,A1,X1,F1,XT1,FT1,2,2,Y1,4,L1,6,
       1 IT1,ER1,P,D)
         WRITE(5,130)X1(1),X1(2)
C        WRITE(2,130)X1(1),X1(2)
  130    FORMAT(5X,'X1(1) = ',G12.5,5X,'X1(2) = ',G12.5)
         DL=ZL(51)-ZL(1)
         READ(1,145)AS,BS,STOICH,CS,SMW
  145    FORMAT(5G12.5)
         READ(1,146)AKO,AKS,AKD,Y,AKT,TREF
  146    FORMAT(6G12.5)
         TREF=(TREF-32.0)/1.8
         IF(TREF.GT.30.0)TREF=30.0
         DRIFT=ZLZ*PDRIF/100.0
         FBLOW=DL/(CC-1.0)-DRIFT
         FMAKE=CC*DL/(CC-1.0)
         IF(FBLOW.LT.0.0)WRITE(5,900)
         IF(FBLOW.LT.0.0)WRITE(2,900)
  900    FORMAT(5X,'DRIFT RATE TOO HIGH')
         DZ=Z/50.0
         AKYA=ZM*GP/Z
         AKYA=AKYA*14.7*((1.0/SMW+1.0/29.0)**0.5)/
       1 (29.0*PT*((1.0/18.0+1.0/29.0)**0.5))
         TC=(TL(1)-32.0)/1.8
         PW=DEXP(16.8060-9442.23/(TL(1)+460.0))
         IF(TC.LT.30.0) DO2IN=(PT-PW)*760.0*0.678/
       1 (14.7*(35.0+TC))
         IF(TC.GE.30.0) DO2IN=(PT-PW)*760.0*0.827/
```

```
      1  (14.7*(49.0+TC))
         FXS=32.0E6*STOICH/18.0
         CONS1=28.3*18.0/(24.0*32.0*1000.0*454.0*
      1  STOICH)
         CONS2=28.3/(24.0*0.454)
         CONS3=CONS1/18.0
         SAREA=SAREA/30.48
         AKT=AKT*1.0E6
         READ(1,155)X2(1),X2(2),X2(3),ER2,IT2,D
  155    FORMAT(3G12.5,/,G12.5,I5,G12.5)
         P=0.0
         NSW=0
         IF(NBS.EQ.1)GO TO 222
         N1=1
         GO TO 232
  222    N1=2
  232    N2=2*N1
         N3=3*N1
         CALL SOLVE(2,FUN2,A2,X2,F2,XT2,FT2,N1,N1,
      1  Y2,N2,L2,N3,IT2,ER2,P,D)
         IF(NBS.NE.1)GO TO 242
         IF(DO2.LT.2.0.AND.NSW.NE.1)GO TO 252
         GO TO 242
  252    N1=3
         NSW=1
         GO TO 232
  242    CONTINUE
         WRITE(5,120)X2(1),X2(2),X2(3)
C        WRITE(2,120)X2(1),X2(2),X2(3)
  120    FORMAT(5X,'X2(1,2,3) = ',3G12.5)
         FM2=FMAKE*CAREA
         WRITE(5,505)FMAKE,FM2,CS
         WRITE(2,505)FMAKE,FM2,CS
  505    FORMAT(/,5X,'LIQUID STREAMS',/,8X,'MAKEUP',/,11X,
      1  'FLOW RATE: ',G11.3,' LB/(SQ FT HR)',/,22X,G11.3,
      2  ' LB/HR',/,11X,'POLLUTANT CONC:  ',G11.3,' PPM')
         FR2=ZLZ*CAREA
         PCI=XS(51)*SMW*1.0E6/18.0
         PCO=XS(1)*SMW*1.0E6/18.0
         Q=ZLZ*CAREA*(TL(51)-TL(1))
         WRITE(5,515)ZLZ,FR2,PCI,XB(51),TL(51),PCO,
      1  XB(1),TL(1),DO2IN,Q,DO2
         WRITE(2,515)ZLZ,FR2,PCI,XB(51),TL(51),PCO,
      1  XB(1),TL(1),DO2IN,Q,DO2
  515    FORMAT(8X,'CIRCULATION',/,11X,'FLOW RATE: ',
      1  G11.3,' LB/(SQ FT HR)',/,22X,G11.3,' LB/HR',/,
      2  11X,'INLET OF COOLING TOWER',/,14X,'POLLUTANT ',
      3  'CONC: ',G9.3,' PPM',/,14X,'BIOMASS CONC: ',
      4  G12.3,'PPM',/,14X,'TEMPERATURE: ',F8.2,'  F',/,
      5  11X,'OUTLET OF COOLING TOWER',/,14X,'POLLUTANT ',
      6  'CONC: ',G9.3,' PPM',/,14X,'BIOMASS CONC: ',G11.3,
      7  ' PPM',/,14X,'TEMPERATURE: ',F8.2,'  F',/,14X,
      8  'OXYGEN CONC: ',G12.3,' PPM',/,11X,'HEAT DUTY: ',
      9  G12.4,' BTU/HR',/,11X,'OXYGEN CONC AT HOLDING BASIN',
      1  ' OUTLET: ',G11.3,' PPM')
         FR1=ZLZ*PDRIF/100.0
         FR2=FR1*CAREA
      PE=PCI*1.0E-6*FR2
      PER=PE/FM2
      BE=XB(51)*1.0E-6*FR2
      BER=BE/FM2
      WRITE(5,525)FR1,FR2,PCI,PE,PER,XB(51),BE,BER
      WRITE(2,525)FR1,FR2,PCI,PE,PER,XB(51),BE,BER
525   FORMAT(8X,'DRIFT',/,11X,'FLOWRATE: ',G13.3,
    1 'LB/(SQ FT HR)',/,22X,G11.3,' LB/HR',11X,
    2 /,11X,'POLLUTANT CONC: ',G11.3,'  PPM',/,11X,
    3 'POLLUTANT EMISSION: ',G11.3,' LB/HR',/,31X,
    4 G11.3,' LB/LB MAKEUP',/,11X,'BIOMASS CONC: ',
    5 G11.3,4X,'PPM',/,11X,'BIOMASS EMISSION: ',G11.3,
    6 ' LB/HR',/,28X,G12.3,' LB/LB MAKEUP')
      FR2=FBLOW*CAREA
      PB=FR2*PCI*1.0E-6
      PBR=PB/FM2
      BB=XB(51)*FR2*1.0E-6
      BBR=BB/FM2
      WRITE(5,535)FBLOW,FR2,PCI,PB,PBR,XB(51),BB,BBR
      WRITE(2,535)FBLOW,FR2,PCI,PB,PBR,XB(51),BB,BBR
535   FORMAT(8X,'BLOWDOWN',/,11X,'FLOW RATE: ',G11.3,
    1 ' LB/(SQ FT HR)',/,22X,G11.3,' LB/HR',/,11X,
    2 'POLLUTANT CONC: ',G12.3,' PPM',/,11X,'POLLUTANT'
    3 ' BLOWDOWN: ',G11.3,' LB/HR',/,31X,G11.3,' LB/LB'
    4 ' MAKEUP',/,11X,'BIOMASS CONC: ',G14.3,' PPM',
    5 /,11X,'BIOMASS BLOWDOWN: ',G12.3,' LB/HR',/,31X,
    6 G11.3,' LB/LB MAKEUP')
      GP2=GP*CAREA
      PCG=YS(51)*1.0E6
      PE=YS(51)*GM(51)*SMW*CAREA
      PER=PE/FM2
      WRITE(5,545)GP,GP2,PCG,PE,PER
      WRITE(2,545)GP,GP2,PCG,PE,PER
545   FORMAT(5X,'GAS STREAM',/,8X,'FLOW RATE: ',
    1 G11.3,' LB/(SQ FT HR)',/,19X,G11.3,' LB/HR',/,8X,
    2 'POLLUTANT CONC: ',G15.3,' PPMV',/,8X,'POLLUTANT',
    3 ' EMISSION: ',G11.3,' LB/HR',/,28X,G11.3,' LB/',
    4 'LB MAKEUP')
      WRITE(5,555)
      WRITE(2,555)
555   FORMAT(5X,'EMISSIONS SUMMARY')
      SIN=FMAKE*CS*1.0E-6
      SEX=FBLOW*XS(51)*SMW/18.0
      R=SEX*100.0/SIN
      WRITE(5,124)R
      WRITE(2,124)R
124   FORMAT(8X,'% OF POLLUTANT REPORT'
    1 ' TO BLOWDOWN: ',6X,F8.2)
      EVOL=GM(51)*YS(51)*SMW
      R2=EVOL*100.0/SIN
      EDRIF=XS(51)*SMW*ZLZ*PDRIF/(18.0*100.0)
      R3=EDRIF*100.0/SIN
      TEVOL=R2+R3
      PBIOX=100.0-R-TEVOL
      BIO=XB(51)*ZLZ*1.0E-6*PDRIF/(100.0*SIN)
      BIOCOL=ZL(51)*XS(51)*SMW/18.0-
    1 ZL(1)*XS(1)*SMW/18.0-EVOL
```

```
CT$MAIN

          PBC=BIOCOL*100.0/SIN
          WRITE(5,134)R2,R3,TEVOL,PBIOX,PBC,BIO
          WRITE(2,134)R2,R3,TEVOL,PBIOX,PBC,BIO
   134    FORMAT(8X,'% POLLUTANT STRIPPED: ',19X,
        1 F8.2,/,8X,'% POLLUTANT EVOLVED WITH'
        2 ' DRIFT: ',6X,F11.2,/,8X,'TOTAL % OF POLLUTANT'
        3 ' EMITTED TO ATMOSPHERE: ',F5.2,/,8X,
        4 '% POLLUTANT BIOOXIDIZED: ',16X,F8.2,/,8X,
        5 '% POLLUTANT BIOOXIDIZED IN TOWER: ',F15.2,/,8X,
        6 'EMISSIONS OF BIOACTIVE MATERIAL: ',
        7 G12.4,/,8X,'( LB./LB. POLLUTANT IN MAKEUP)')
          STOP
          END
```

```
C
C
            SUBROUTINE FUN1(N,X1,F1)
            IMPLICIT DOUBLE PRECISION (A-H,O-Z)
            DIMENSION X1(2),F1(2)
            COMMON PT,XHO,YO,GP,TLZ,ZLZ,ZM,ZL(52),TL(52),
          1 GM(52),DZM,PDRIF,XS(52),XB(52),YS(52),CONS1,
          2 CONS2,FXS,AKO,TREF,DZ,AKYA,AS,BS,FL,SAREA,AKT,
          3 AKS,Y,AKD,CONS3,VH,CAREA,FMAKE,CS,SMW,FBLOW
          4 ,DO2IN,DO2,NBS,NSW
            ZL(1)=X1(1)
            TL(1)=X1(2)
            XHO=XHO
            YO=YO
            GM(1)=GP*(1.0/29.0+YO/18.0)
            DO 101 I=1,50
            PH2O=DEXP(16.8060-9442.23/(460.0+TL(I)))
            R=PH2O/PT
            YIO=R*18.0/(29.0*(1.0-R))
            XHIO=0.24*(TL(I)-32.0)+YIO*0.5*(TL(I)-32.0)
          1 +YIO*1075.8
            AH=DZM*(XHIO-XHO)
            XHN=XHO+AH
            AY=DZM*(YIO-YO)
            YN=YO+AY
            ZL(I+1)=ZL(I)+GP*(YN-YO)
            TL(I+1)=(ZL(I)*TL(I)+GP*(XHN-XHO))/ZL(I+1)
            PH2O=DEXP(16.8060-9442.23/(460.0+TL(I+1)))
            R=PH2O/PT
            YIN=R*18.0/(29.0*(1.0-R))
            XHIN=0.24*(TL(I+1)-32.0)+YIN*0.5*(TL(I+1)-32.0)
          1 +YIN*1075.8
            BH=DZM*(XHIN-XHN)
            XHN=XHO+0.5*(AH+BH)
            BY=DZM*(YIN-YN)
            YN=YO+0.5*(AY+BY)
            ZL(I+1)=ZL(I)+GP*(YN-YO)
            TL(I+1)=(ZL(I)*TL(I)+GP*(XHN-XHO))/ZL(I+1)
            GM(I+1)=GP*(1.0/29.0+YN/18.0)
            XHO=XHN
            YO=YN
    101     CONTINUE
            F1(1)=TL(51)-TLZ
            F1(2)=ZL(51)-ZLZ*(1.0-PDRIF/100.0)
            RETURN
            END
```

```
C
C
        SUBROUTINE FUN2(N,X2,F2)
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        DIMENSION X2(3),F2(3)
        COMMON PT,XHO,YO,GP,TLZ,ZLZ,ZM,ZL(52),TL(52),
     1  GM(52),DZM,PDRIF,XS(52),XB(52),YS(52),CONS1,
     2  CONS2,FXS,AKO,TREF,DZ,AKYA,AS,BS,FL,SAREA,AKT,
     3  AKS,Y,AKD,CONS3,VH,CAREA,FMAKE,CS,SMW,FBLOW
     4  ,DO2IN,DO2,NBS,NSW
        XS(1)=X2(1)
        XB(1)=X2(2)
        IF(NBS.EQ.0)XB(1)=0.0
        DO2=X2(3)
        FAKT=1.0
        YS(1)=0.0
        IF(NBS.EQ.0)FAKT=0.0
        DO 1   I=1,50
        TC=(TL(I)-32.0)/1.8
        IF(TC.GT.30.0)TC=30.0
        AK=AKO*((1.035)**(TC-20.0))/((1.035)**
     1  (TREF-20.0))
        ALXS=DZ*18.0*AKYA*(H(TL(I),AS,BS)*XS(I)/
     1  PT -YS(I))+CONS1*DZ*(FL*XB(I)+SAREA*AKT*FAKT)*
     2  (AK*FXS*XS(I))/(AKS+FXS*XS(I))
        XS(I+1)=(ZL(I)*XS(I)+ALXS)/ZL(I+1)
        AGYS=DZ*AKYA*(H(TL(I),AS,BS)*XS(I)/PT-YS(I))
        YS(I+1)=(GM(I)*YS(I)+AGYS)/GM(I+1)
        ALXB=-CONS2*DZ*(FL*XB(I)+SAREA*AKT*FAKT)*(Y*AK*
     1  FXS*XS(I)/(AKS+FXS*XS(I))-AKD)
        XB(I+1)=(ZL(I)*XB(I)+ALXB)/ZL(I+1)
        IF(NBS.EQ.0)XB(I+1)=0.0
        TC=(TL(I+1)-32.0)/1.8
        IF(TC.GE.30.0)TC=30.0
        AK=AKO*((1.035)**(TC-20.0))/((1.035)**
     1  (TREF-20.0))
        BLXS=18.0*DZ*AKYA*(H(TL(I+1),AS,BS)*
     1  XS(I+1)/PT-YS(I+1))+CONS1*DZ*(FL*XB(I+1)+
     2  SAREA*AKT*FAKT)*(AK*FXS*XS(I+1))/(AKS+FXS*XS(I+1))
        XS(I+1)=(ZL(I)*XS(I)+0.5*(ALXS+BLXS))/
     1  ZL(I+1)
        BGYS=DZ*AKYA*(H(TL(I+1),AS,BS)*XS(I+1)/
     1  PT-YS(I+1))
        YS(I+1)=(GM(I)*YS(I)+0.5*(AGYS+BGYS))/
     1  GM(I+1)
        BLXB=-CONS2*DZ*(FL*XB(I+1)+SAREA*AKT*FAKT)*(Y*AK*
     1  FXS*XS(I+1)/(AKS+FXS*XS(I+1))-AKD)
        XB(I+1)=(ZL(I)*XB(I)+0.5*(ALXB+BLXB))/ZL(I+1)
        IF(NBS.EQ.0)XB(I+1)=0.0
    1   CONTINUE
        RATIO=1.0
        IF(DO2.LT.2.0) RATIO=DO2/2.0
        IF(NSW.EQ.0)RATIO=1.0
        TC=(TL(1)-32.0)/1.8
        IF(TC.GT.30.0)TC=30.0
        AK=AKO*((1.035)**(TC-20.0))/((1.035)**
     1  (TREF-20.0))
```

```
FUN2

           RS=RATIO*VH*AK*XB(51)*FXS*XS(51)/(AKS+
         1 FXS*XS(51))
           F2(1)=(ZL(1)*CAREA*XS(1)/18.0+FMAKE*CAREA*
         1 CS*1.0E-6/SMW)-((ZLZ+FBLOW)*CAREA*XS(51)/
         2 18.0+RS*CONS3)
           IF(NBS.EQ.0)GO TO 202
           F2(2)=(ZL(1)*CAREA*XB(1)*0.454+28.3*Y*RS/
         1 24.0)-((ZLZ+FBLOW)*CAREA*XB(51)*0.454+
         2 28.3*AKD*XB(51)*VH/24.0)
           IF (NSW.EQ.1)GO TO 222
           DO2=(ZL(1)*DO2IN*1.0E-6*CAREA-28.3*RS/
         1 (24.0*1000.0*454.0))/((ZLZ+FBLOW)*1.0E-6*
         2 CAREA)
           GO TO 202
     222   F2(3)=(ZL(1)*DO2IN*1.0E-6*CAREA)-((ZLZ+
         1 FBLOW)*DO2*1.0E-6*CAREA+28.3*RS/(24.0*
         2 1000.0*454.0))
     202   RETURN
           END
```

```
   C
   C
           FUNCTION H(T,A,B)
           IMPLICIT DOUBLE PRECISION (A-H,O-Z)
           H=DEXP(A+B/(T+460.0))
           RETURN
           END
```

```
      SUBROUTINE SOLVE (IN,FUNCS,A,X,F,XT,FT,N,M,Y,N2,L,N3,IT,E,P,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION A(N,M),X(N),F(N),XT(N),FT(N),Y(N2),L(N3),PHI(3),VT(3)
      LOGICAL B(9)
      IF (D.GT.256.) D=-1.
      B(9)=D.GE.0.
      T=128.
      DO 120 II=1,8
      I=9-II
      D=D-T
      IF (D.LT.-.001) GO TO 110
      B(I)=.TRUE.
      GO TO 120
  110 D=D+T
      B(I)=.FALSE.
  120 T=T/2.
      IF (IN.NE.2) GO TO 300
      IF (E.EQ.0.) E=.001
      IF (IT.EQ.0) IT=50
      ERR2=E**2
      CALL FUNCS (N,X,F)
      IF (B(5).OR.B(6)) WRITE (5,850) ((I,X(I),I,F(I)),I=1,N)
      ERROLD=0.
      DO 210 I=1,N
      I1=I+N
      ERROLD=ERROLD+F(I)**2
      Y(I1)=X(I)/10000.
  210 XT(I)=X(I)
      IF (B(2).OR.B(3)) WRITE (5,820) ERROLD
      DO 230 I=1,N
      I1=I+N
      XT(I)=X(I)+Y(I1)
      CALL FUNCS (N,XT,FT)
      DO 220 J=1,N
  220 A(J,I)=(FT(J)-F(J))/Y(I1)
  230 XT(I)=X(I)
  300 PIVMIN=1.D30
      D=1.
      DO 380 K=1,N
      K1=K+N
      KM1=K-1
      K1M1=K1-1
      PIVOT=0.
      DO 330 I=1,N
      DO 330 J=1,N
      IF (K.EQ.1) GO TO 320
      DO 310 ISCAN=1,KM1
      DO 310 JSCAN=1,KM1
      JSCAN1=JSCAN+N
      IF (I.EQ.L(ISCAN)) GO TO 330
      IF (J.EQ.L(JSCAN1)) GO TO 330
  310 CONTINUE
  320 IF (DABS(A(I,J)).LE.DABS(PIVOT)) GO TO 330
      PIVOT=A(I,J)
      L(K)=I
      L(K1)=J
  330 CONTINUE
```

SOLVE

```
      ABSPIV=DABS(PIVOT)
      IF (ABSPIV.LT.PIVMIN) PIVMIN=ABSPIV
      IF (P.EQ.0..OR.ABSPIV.GE.P) GO TO 340
      D=0.
      IF (B(9)) WRITE (5,910)
      IF (.NOT.B(9)) WRITE (5,910)
      RETURN
  340 IROWK=L(K)
      JCOLK=L(K1)
      D=D*PIVOT
      IF (B(8)) WRITE (5,800)
      DO 350 I=1,N
      IF (B(8)) WRITE (5,880) ((I,J,A(I,J)),J=1,M)
  350 IF (B(8).AND.M.GT.5.AND.I.NE.N) WRITE (5,800)
      IF (B(8)) WRITE (5,890) K,PIVOT,IROWK,JCOLK
      DO 360 J=1,M
  360 A(IROWK,J)=A(IROWK,J)/PIVOT
      A(IROWK,JCOLK)=1./PIVOT
      DO 380 I=1,N
      AIJCK=A(I,JCOLK)
      IF (I.EQ.IROWK) GO TO 380
      A(I,JCOLK)=-AIJCK/PIVOT
      DO 370 J=1,M
  370 IF (J.NE.JCOLK) A(I,J)=A(I,J)-AIJCK*A(IROWK,J)
  380 CONTINUE
      IF (B(8)) WRITE (5,800)
      DO 390 I=1,N
      IF (B(8)) WRITE (5,880) ((I,J,A(I,J)),J=1,M)
  390 IF (B(8).AND.M.GT.5.AND.I.NE.N) WRITE (5,800)
      DO 400 I=1,N
      I1=I+N
      IROWI=L(I)
      JCOLI=L(I1)
      IROWI2=IROWI+N2
      L(IROWI2)=JCOLI
  400 IF (IN.GE.0.AND.IN.NE.2) X(JCOLI)=-A(IROWI,M)
      INTCH=0
      NM1=N-1
      DO 410 I=1,NM1
      I2=I+N2
      IP1=I+1
      DO 410 J=IP1,N
      J2=J+N2
      IF(N .EQ. 1)GO TO 410
      IF (L(J2).GE.L(I2)) GO TO 410
      JTEMP=L(J2)
      L(J2)=L(I2)
      L(I2)=JTEMP
      INTCH=INTCH+1
  410 CONTINUE
      IF (INTCH/2*2.NE.INTCH) D=-D
      IF (IN.GT.0.AND.IN.NE.2) GO TO 460
      DO 430 J=1,N
      DO 420 I=1,N
      I1=I+N
      IROWI=L(I)
      JCOLI=L(I1)
```

```
 420     Y(JCOLI)=A(IROWI,J)
         DO 430 I=1,N
 430     A(I,J)=Y(I)
         DO 450 I=1,N
         DO 440 J=1,N
         J1=J+N
         IROWJ=L(J)
         JCOLJ=L(J1)
 440     Y(IROWJ)=A(I,JCOLJ)
         DO 450 J=1,N
 450     A(I,J)=Y(J)
 460     IF (P.EQ.0.) P=PIVMIN
         IF (IN.NE.2) RETURN
         DO 510 I=1,N
         DO 510 J=1,N
 510     A(I,J)=A(I,J)*-1.
         DO 610 K=1,IT
         IF (B(4)) WRITE (5,840) K
         IF (B(7)) WRITE (5,800)
         DO 520 I=1,N
         IF (B(7)) WRITE (5,870) ((I,J,A(I,J)),J=1,N)
 520     IF (B(7).AND.M.GT.5.AND.I.NE.N) WRITE (5,800)
         DO 530 I=1,N
         I1=I+N
         Y(I1)=0
         DO 530 J=1,N
 530     Y(I1)=Y(I1)+A(I,J)*F(J)
         T=1.
         TOLD=0.
         ITER=0
 540     DO 550 I=1,N
         I1=I+N
 550     XT(I)=X(I)+(T-TOLD)*Y(I1)
         CALL FUNCS (N,XT,FT)
         IF (B(6)) WRITE (5,860) ((I,XT(I),I,FT(I)),I=1,N)
         ERRNEW=0.
         DO 560 I=1,N
 560     ERRNEW=ERRNEW+FT(I)**2
         IF (B(3)) WRITE (5,830) ERRNEW
         IF (ERRNEW.GE.ERROLD) GO TO 620
         IF (ERRNEW.LT.ERR2) GO TO 720
 570     DO 580 I=1,N
         Y(I)=FT(I)-F(I)
         X(I)=XT(I)
 580     F(I)=FT(I)
         ERROLD=ERRNEW
         DO 590 I=1,N
         XT(I)=0.
         DO 590 J=1,N
 590     XT(I)=XT(I)+A(I,J)*Y(J)
         DENOM=0.
         DO 600 I=1,N
         I1=I+N
         DENOM=DENOM+Y(I1)*XT(I)
         FT(I)=XT(I)+T*Y(I1)
         Y(I)=0.
         DO 600 J=1,N
```

```
        J1=J+N
  600   Y(I)=Y(I)+Y(J1)*A(J,I)
        DO 610 I=1,N
        DO 610 J=1,N
  610   A(I,J)=A(I,J)-FT(I)*Y(J)/DENOM
        IF (B(5).AND..NOT.B(6)) WRITE (5,860) ((I,XT(I),I,FT(I)),I=1,N)
        IF (B(2).AND..NOT.B(3)) WRITE (5,830) ERRNEW
        IF (B(9)) WRITE (5,920) IT
        IF (.NOT.B(9)) WRITE (5,920) IT
        RETURN
  620   ITER=ITER+1
        IF (ITER.LE.10) GO TO 630
        IF (B(1)) WRITE (5,810) K
        GO TO 570
  630   IF (ITER.NE.1) GO TO 640
        VT(1)=0.
        VT(3)=1.
        PHI(1)=ERROLD
        PHI(3)=ERRNEW
        XX=ERRNEW/ERROLD
        T=(DSQRT(1.+6.*XX)-1.)/3./XX
        KL=1
        KM=2
        KH=3
        KI=2
        GO TO 710
  640   PHI(KJ)=ERRNEW
        XW=VT(2)-VT(3)
        XX=VT(3)-VT(1)
        XY=VT(1)-VT(2)
        XW=-(PHI(1)*XW+PHI(2)*XX+PHI(3)*XY)/XW/XX/XY
        XX=(PHI(1)-PHI(2))/XY-(VT(1)+VT(2))*XW
        TOLD=T
        IF (XW.LE.0.) GO TO 650
        T=-XX/XW/2.
        GO TO 670
  650   IF (PHI(KH).LE.PHI(KL)) GO TO 660
        T=3.*VT(KL)-2.*VT(KM)
        GO TO 670
  660   T=3.*VT(KH)-2.*VT(KM)
  670   IF (T.LE.VT(KH)) GO TO 680
        KI=KL
        KL=KM
        KM=KH
        KH=KI
        GO TO 710
  680   IF (T.GE.VT(KL)) GO TO 690
        KI=KH
        KH=KM
        KM=KL
        KL=KI
        GO TO 710
  690   IF (T.LE.VT(KM)) GO TO 700
        KI=KL
        KL=KM
        KM=KI
        GO TO 710
```

```
 700    KI=KH
        KH=KM
        KM=KI
 710    KJ=KI
        VT(KI)=T
        GO TO 540
 720    DO 730 I=1,N
 730    X(I)=XT(I)
        IF (B(5).AND..NOT.B(6)) WRITE (5,860) ((I,XT(I),I,FT(I)),I=1,N)
        IF (B(2).AND..NOT.B(3)) WRITE (5,830) ERRNEW
        IF (B(9)) WRITE (5,900) K
        RETURN
 800    FORMAT (1H )
 810    FORMAT (32HOTHE NORM WAS NOT REDUCED IN THE,I5,13HTH ITERATION.)
 820    FORMAT (9HOERROLD =,G14.6)
 830    FORMAT (9HOERRNEW =,G14.6)
 840    FORMAT (12HOITERATION =,I5)
 850    FORMAT (1H /(6H XOLD(,I2,3H) =,G14.6,4X,5HFOLD(,I2,3H) =,G14.6))
 860    FORMAT (1H /(6H XNEW(,I2,3H) =,G14.6,4X,5HFNEW(,I2,3H) =,G14.6))
 870    FORMAT (3H H(,I2,1H,,I2,3H) =,G14.6:,4X,2HH(,I2,1H,,
     1  I2,3H) =,G14.6:,4X,2HH(,I2,1H,,I2,3H) =,G14.6)
 880    FORMAT (3H A(,I2,1H,,I2,3H) =,G14.6:,4X,2HA(,I2,1H,,
     1  I2,3H) =,G14.6:,4X,2HA(,I2,1H,,I2,3H) =,G14.6)
 890    FORMAT (7HOPASS =,I3,5X,7HPIVOT =,G14.6,5X,7HIROWK =,I3,5X,
     1  7HJCOLK =,I3)
 900    FORMAT (19HOSOLVE CONVERGED IN,I5,12H ITERATIONS.,/)
 910    FORMAT (32HOCOEFFICIENT MATRIX IS SINGULAR.,/)
 920    FORMAT (26HOSOLVE DID NOT CONVERGE IN,I5,12H ITERATIONS.,/)
        END
```

# APPENDIX B. ENTHALPY OF SATURATED AIR

| Temperature °F | Enthalpy Btu/lb dry air | Temperature°F | Enthalpy Btu/lb dry air |
|---|---|---|---|
| 70 | 34.09 | 106 | 83.42 |
| 71 | 34.95 | 107 | 85.56 |
| 72 | 35.83 | 108 | 87.76 |
| 73 | 36.74 | 109 | 90.03 |
| 74 | 37.66 | 110 | 92.34 |
| 75 | 38.61 | 111 | 94.72 |
| 76 | 39.57 | 112 | 97.18 |
| 77 | 40.57 | 113 | 99.71 |
| 78 | 41.58 | 114 | 102.31 |
| 79 | 42.62 | 115 | 104.98 |
| 80 | 43.69 | 115 | 104.98 |
| 81 | 44.78 | 116 | 107.73 |
| 82 | 45.90 | 117 | 110.55 |
| 83 | 47.04 | 118 | 113.46 |
| 84 | 48.22 | 119 | 116.46 |
| 85 | 49.43 | 120 | 119.54 |
| 86 | 50.66 | 121 | 122.72 |
| 87 | 51.93 | 122 | 125.98 |
| 88 | 53.23 | 123 | 129.35 |
| 89 | 54.56 | 124 | 132.80 |
| 90 | 55.93 | 125 | 136.4 |
| 91 | 57.33 | 126 | 140.1 |
| 92 | 58.78 | 127 | 143.9 |
| 93 | 60.25 | 128 | 147.8 |
| 94 | 61.77 | 129 | 151.8 |
| 95 | 63.32 | 130 | 155.9 |
| 96 | 64.92 | 131 | 160.3 |
| 97 | 66.55 | 132 | 164.7 |
| 98 | 68.23 | 133 | 169.3 |
| 99 | 69.96 | 134 | 174.0 |
| 100 | 71.73 | 135 | 178.9 |
| 101 | 73.55 | 136 | 183.9 |
| 102 | 75.42 | 137 | 189.0 |
| 103 | 77.34 | 138 | 194.4 |
| 104 | 79.32 | 139 | 199.9 |
| 105 | 81.34 | 140 | 205.7 |

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# APPENDIX C. TEMPERATURE DATA FROM SELECTED TESTS IN THE FIVE CENTIMETER COOLING TOWER

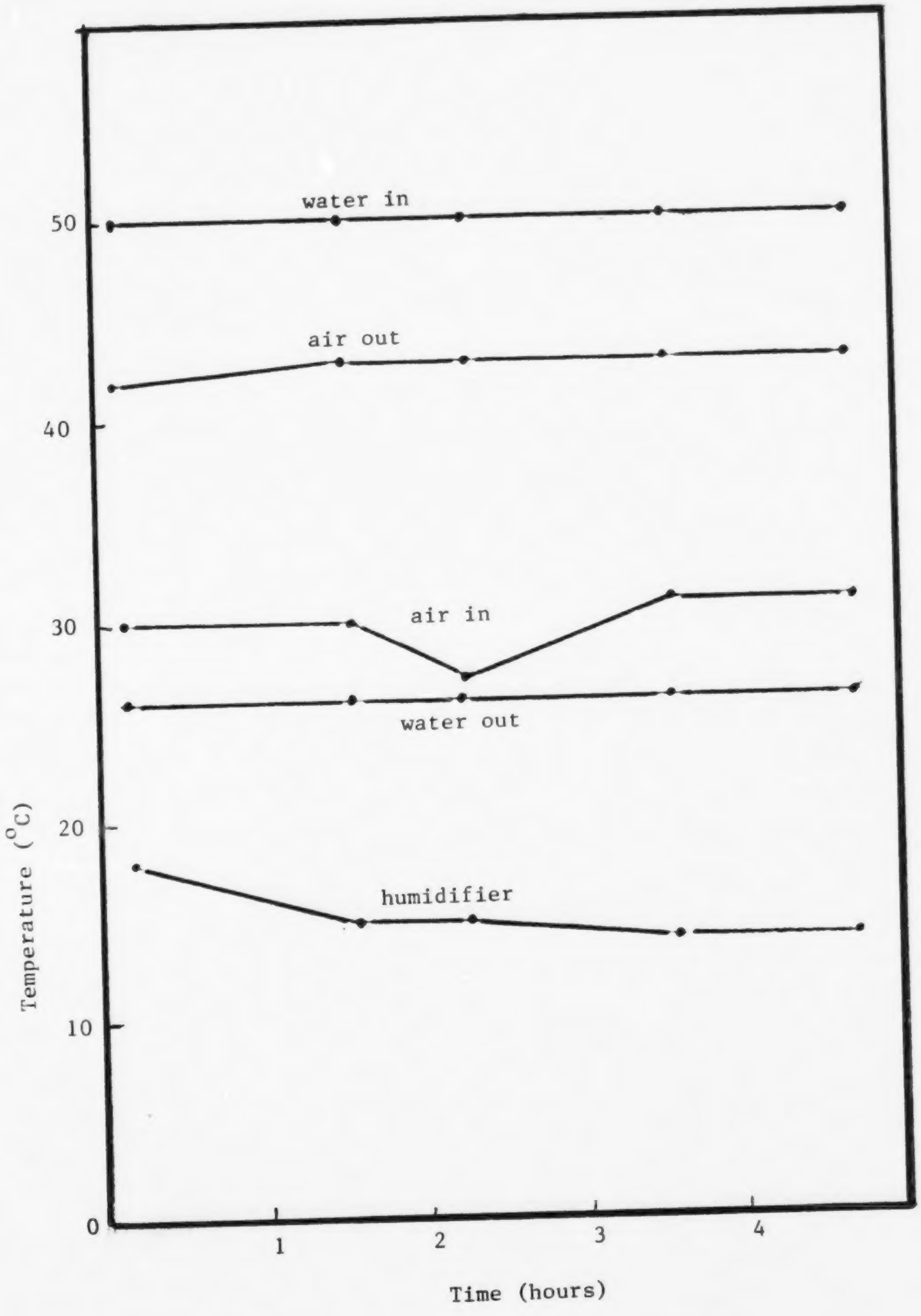

Figure C-1. Temperature Profile -- Test 9

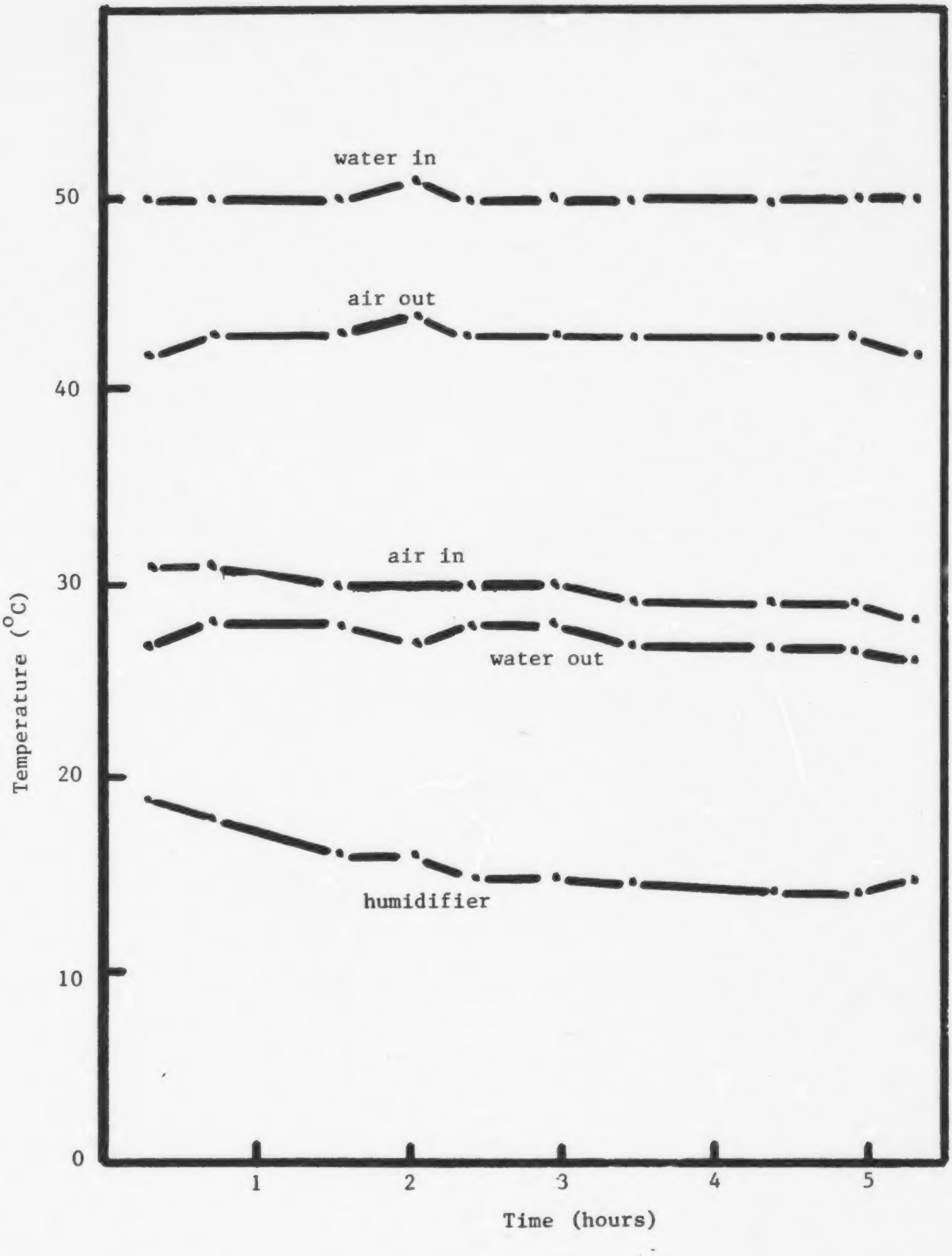

Figure C-2. Temperature Profile - Test 10

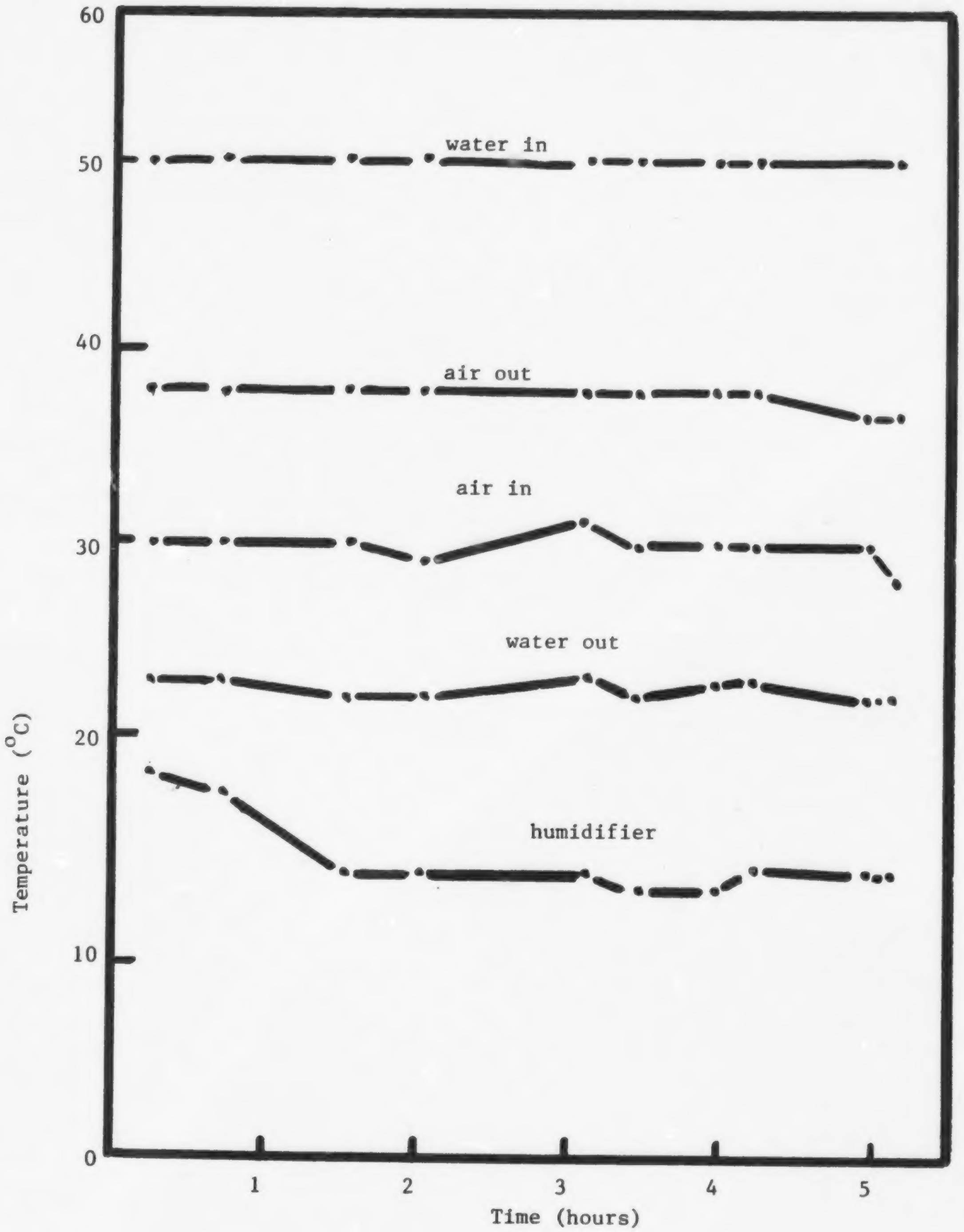

Figure C-3. Temperature Profile - Test 11

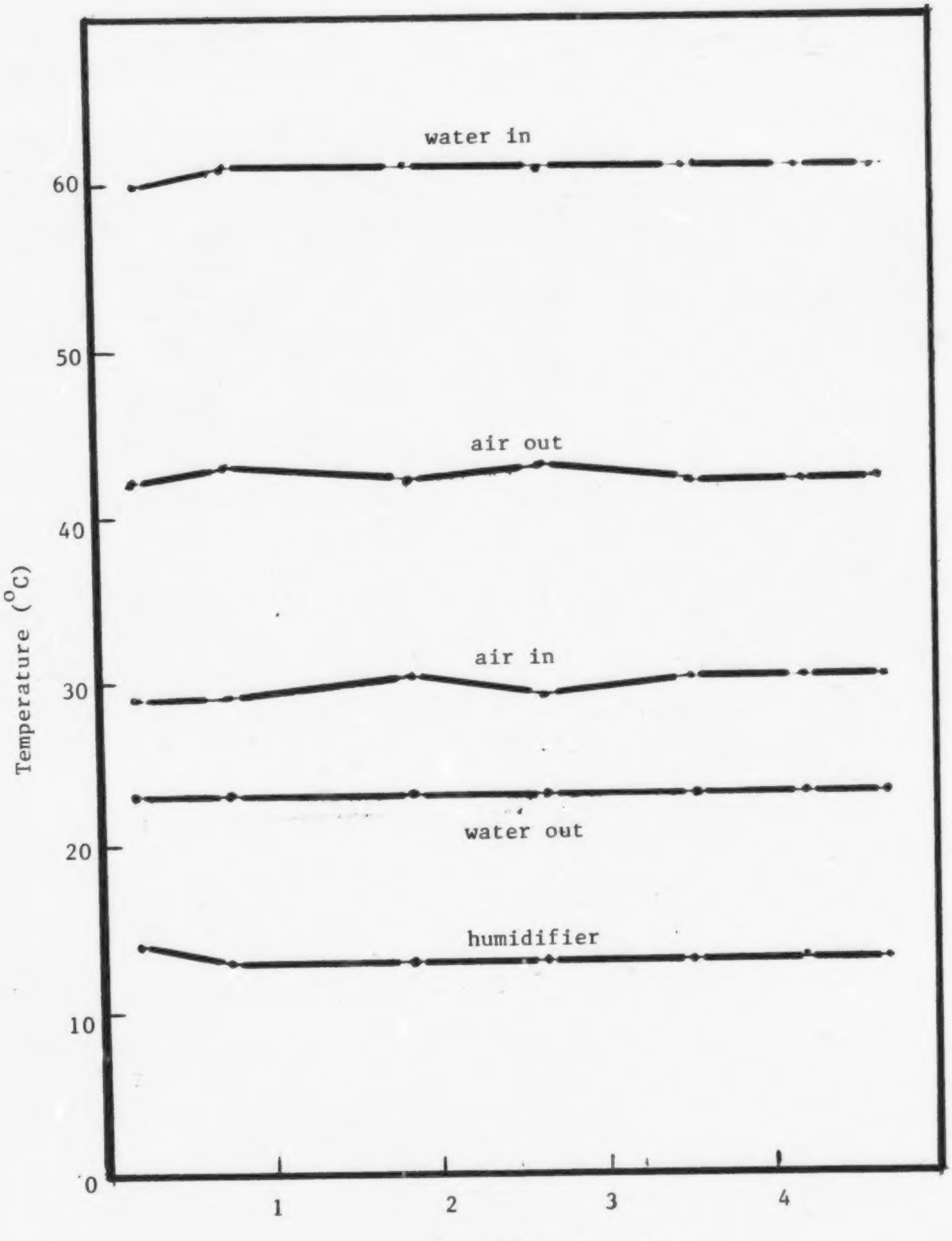

Figure C-4. Temperature Profile - Test 12

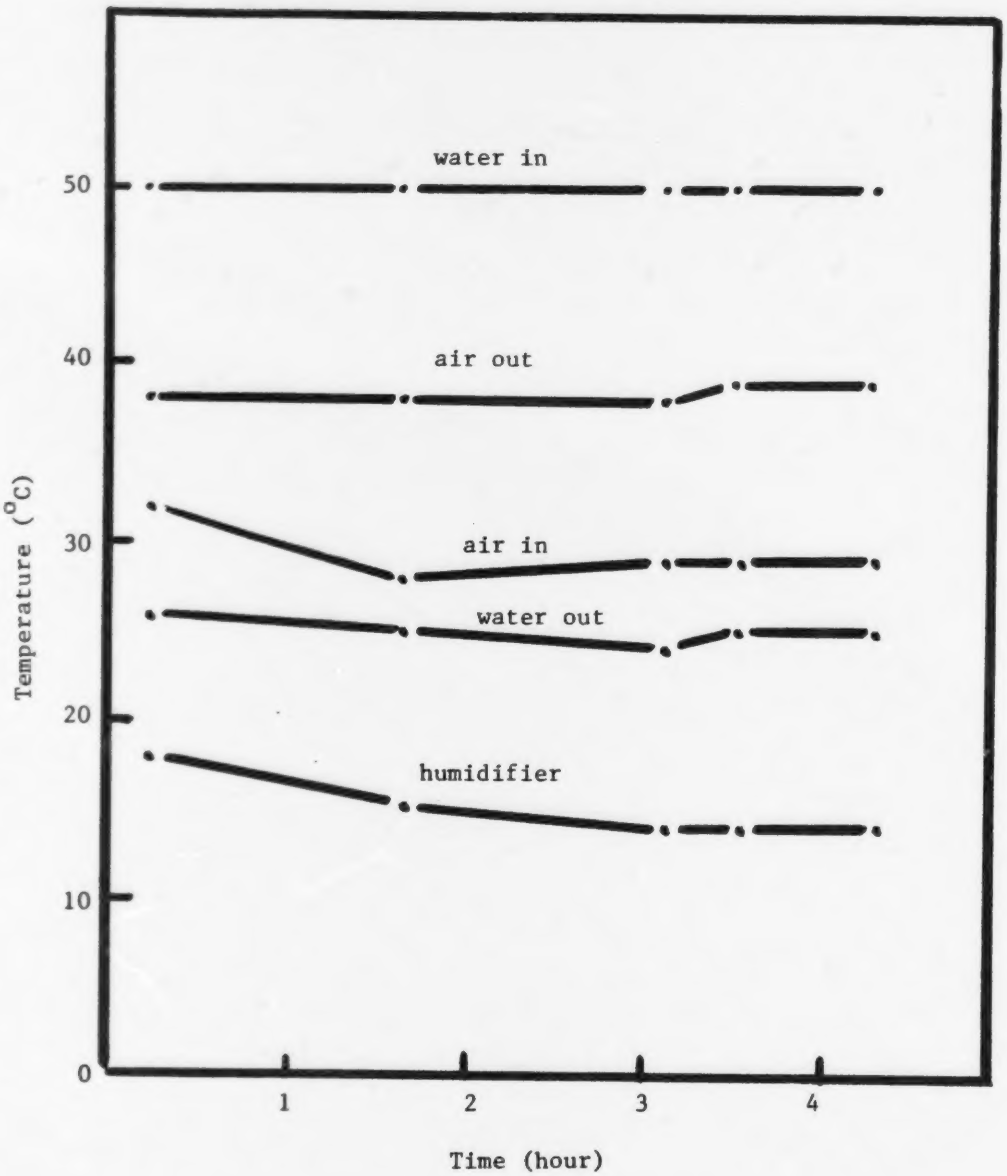

Figure C-5. Temperature Profile - Test 13

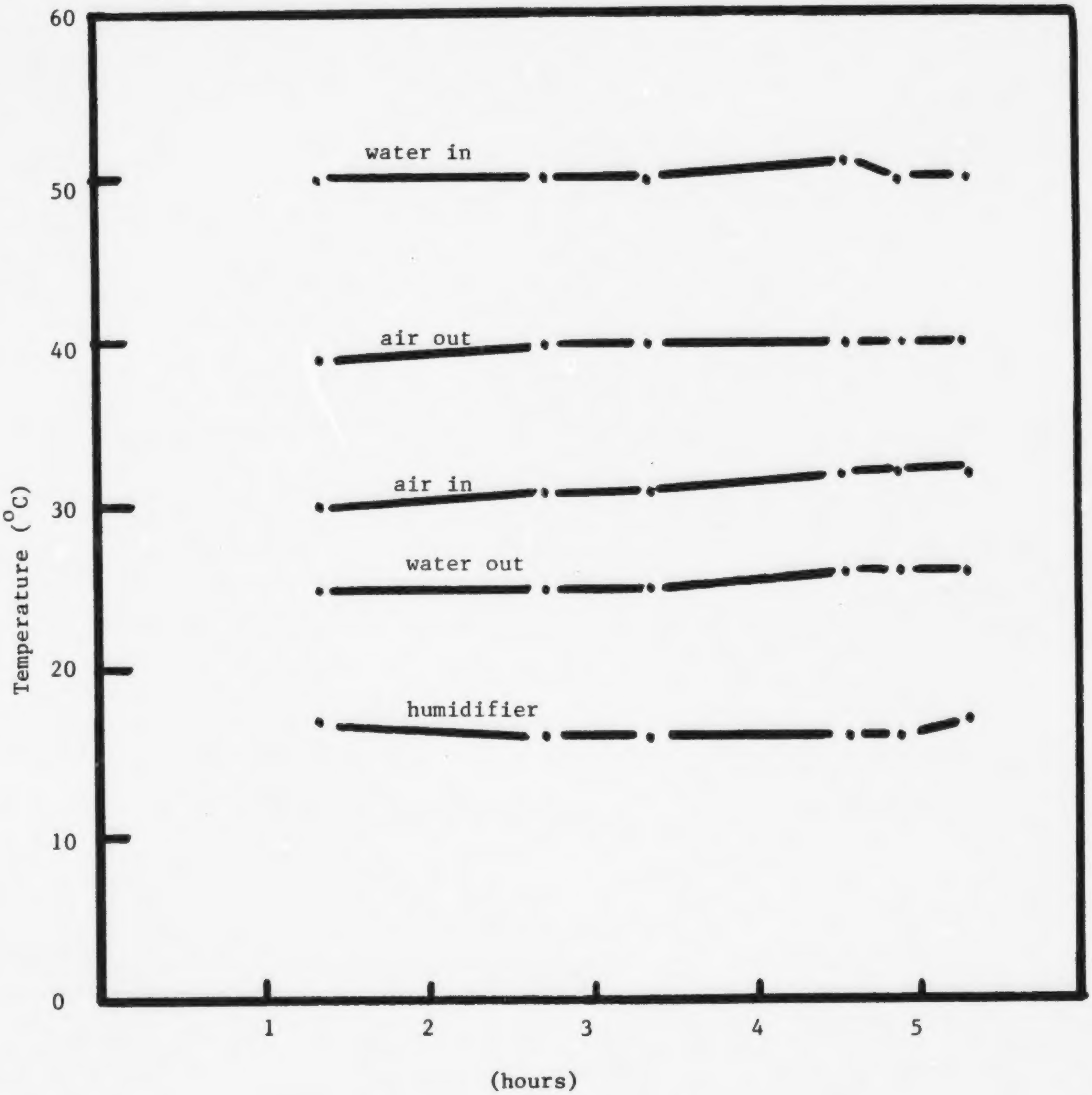

Figure C-6. Temperature Profile - Test 14

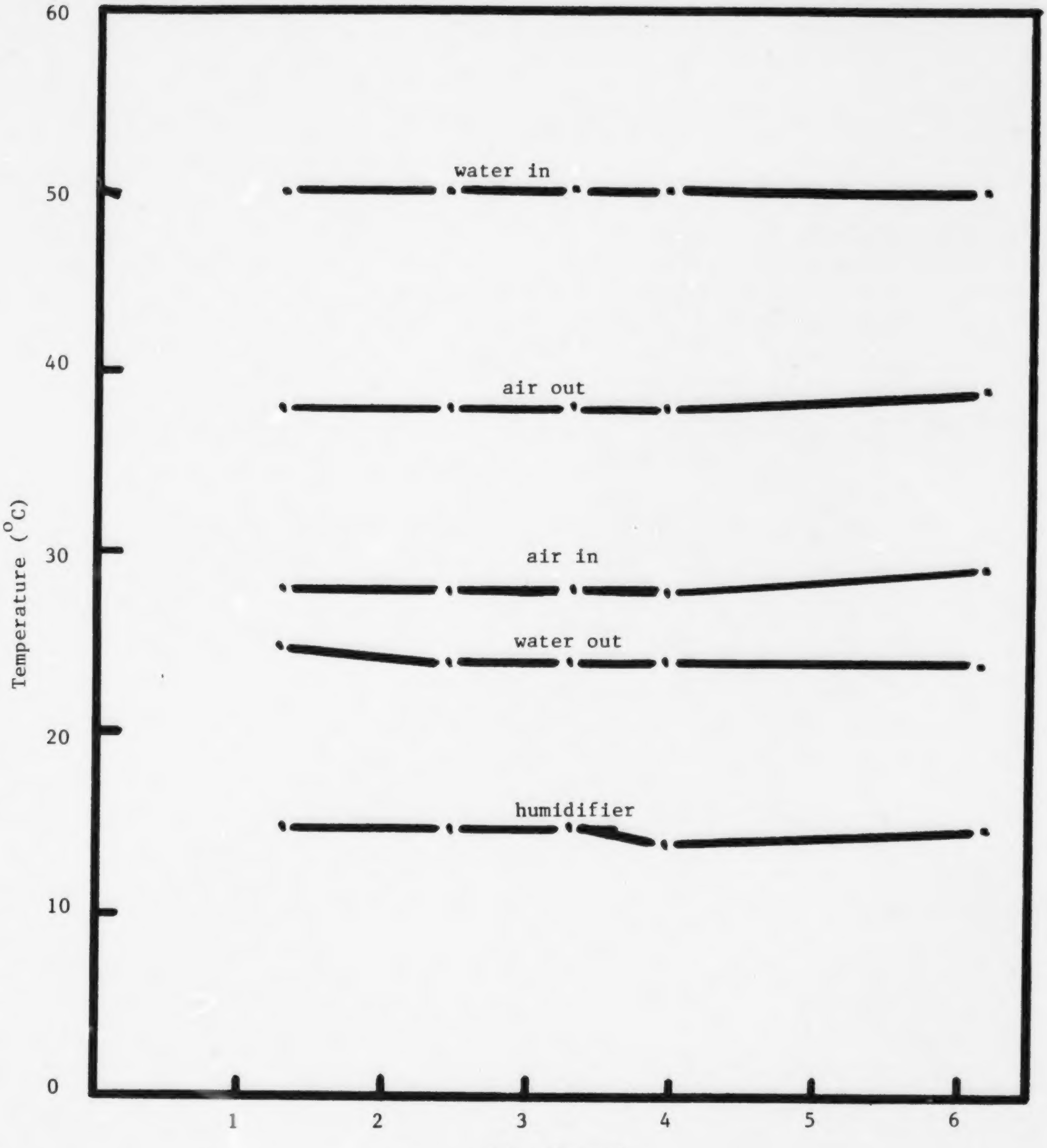

Figure C-7. Temperature Profile - Test 15

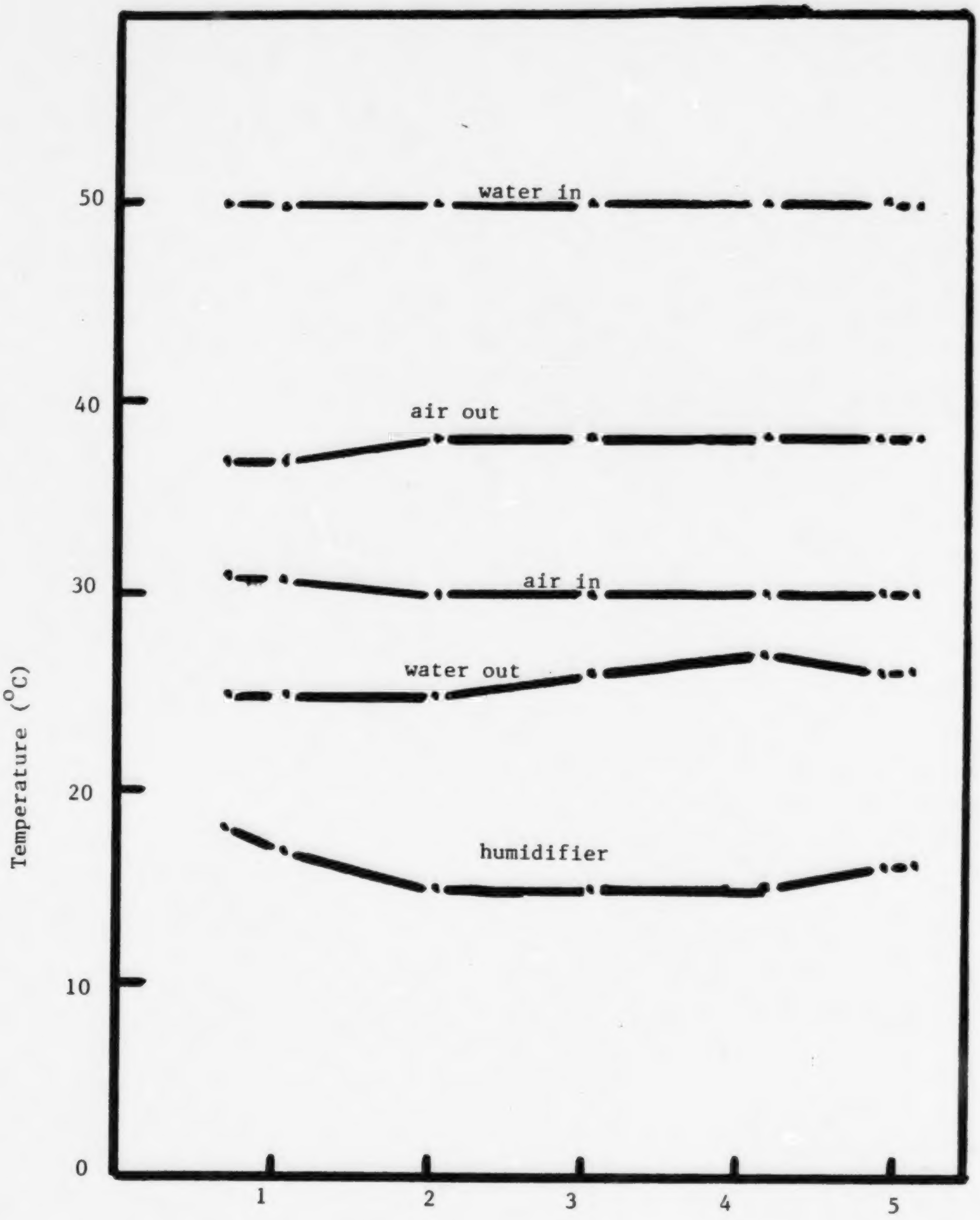

Figure C-8. Temperature Profile - Test 16

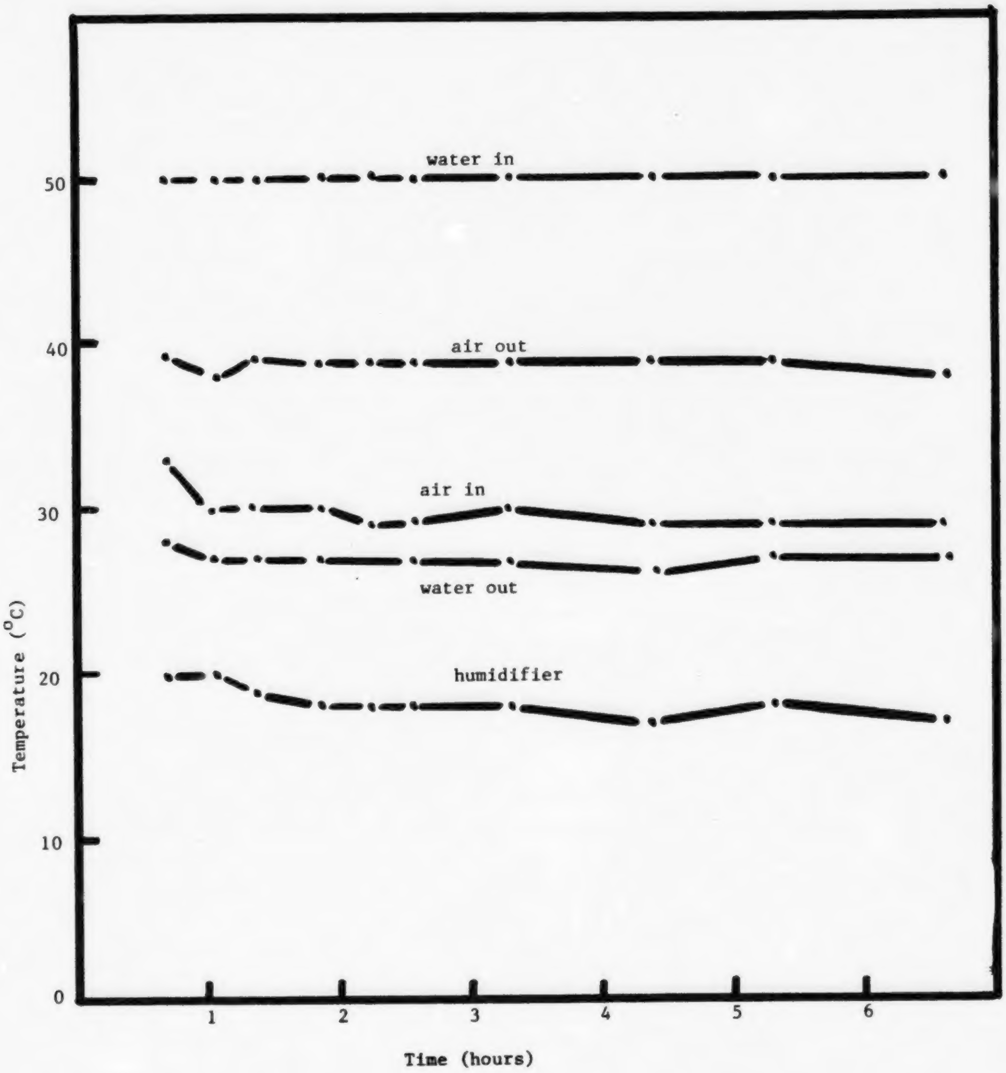

Figure C-9. Temperature Profile - Test 17

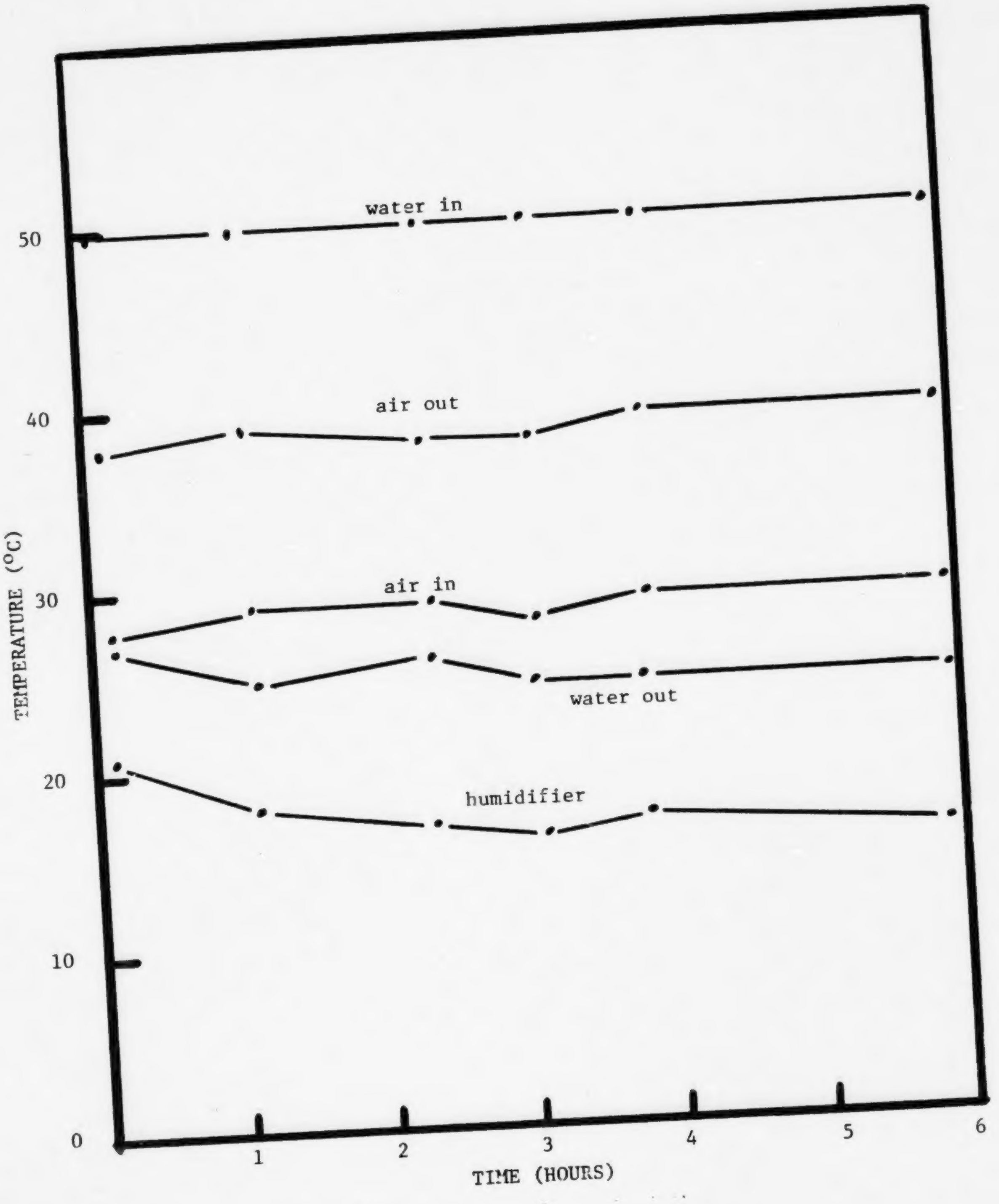

Figure C-10. Temperature Profile - Test 18

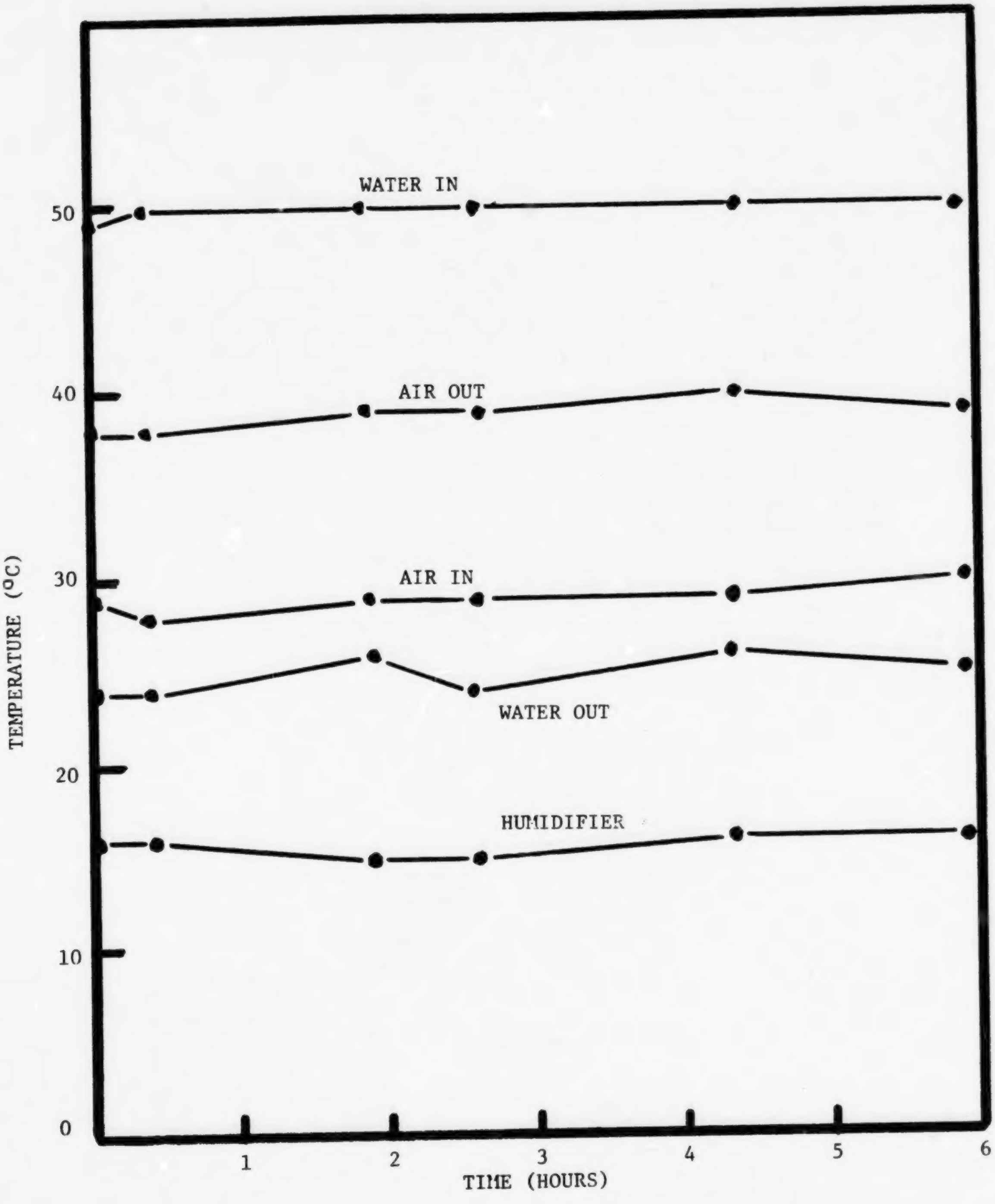

Figure C-11. Temperature Profile - Test 19

# APPENDIX D

# APPROACH TO STEADY STATE OF ORGANIC COMPOUND RECOVERIES IN BLOWDOWN FROM THE FIVE CENTIMETER DIAMETER COOLING TOWER

Tests in the five centimeter cooling tower were conducted over a period of approximately seven hours. The data reported in Section 4 were based on final concentrations after the circulating water concentration had approached steady state. Once a test was started temperatures in the system took about thirty minutes to stabilize. From this point a trial and error procedure of adjusting the makeup flow rate to obtain the desired cycles of concentration required an additional one to two hours. For experimental purposes, this time was designated as the beginning of the data taking period.

Tests were continued for approximately five hours from this point to allow liquid concentrations to stabilize. Because of the dynamics of the system, including changes in ambient temperature which affected heat losses from the tower, cycles of concentration still varied slightly over this period. Intermediate adjustments to makeup flow rate were made to hold the cycles of concentration as constant as possible. Intermediate blowdown recoveries based on samples taken before the final "steady state" sample were calculated to confirm that steady state had been reached. These data are shown in Table D-1 through D-11.

## TABLE D-1. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 9)

| Time | | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|---|
| 0:00 | mg/L | 171 | 2880 | 243 | 15 | 2.44 | --- |
| 0:25 | mg/L | 145 | 4580 | 81 | 1.7 | 2.5 | 1.5 |
| | recovery (%) | 57 | 100+ | 22 | 7.6 | 69 | --- |
| 4:00 | mg/L | 138 | 4400 | 26 | 1.2 | 1.5 | 2.7 |
| | recovery (%) | 30 | 56 | 4.0 | 3.0 | 23 | --- |
| 5:00 | mg/L | 118 | 3300 | 25 | 2.4 | 2.5 | 2.7 |
| | recovery (%) | 26 | 42 | 3.8 | 5.9 | 39 | --- |

TABLE D-2. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 10)

| Time | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|
| 0:00 mg/L | 164 | 2170 | 234 | 9.5 | 1.1 | --- |
| 3:00-4:00 mg/L | 132 | 8490 | 11 | 0.7 | ND | 10.1 |
| recovery (%) | 8.0 | 39 | 0.5 | 0.7 | 0 | --- |
| 4:00-5:00 mg/L | 97 | 7280 | 13 | 0.6 | ND | 9.5 |
| recovery (%) | 6.2 | 35 | 0.6 | 0.7 | 0 | --- |
| 5:00-5:25 mg/L | 142 | 7100 | 23 | 4.8 | ND | 9.8 |
| recovery (%) | 8.8 | 33 | 1.0 | 5.1 | 0 | --- |

TABLE D-3. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 11)

| Time | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|
| 0:00 mg/L | 160 | 2500 | 241 | 12 | 26 | --- |
| 2:00-3:00 mg/L | 120 | 5000 | 6.6 | 0.6 | ND | 9.8 |
| recovery (%) | 7.7 | 20 | 0.2 | 0.5 | 0.0 | --- |
| 3:00-4:00 mg/L | 114 | 2930 | 5.7 | 0.8 | ND | 7.8 |
| recovery (%) | 9.1 | 15 | 0.3 | 0.9 | 0.0 | --- |
| 4:00-4:45 mg/L | 116 | 3720 | 8.9 | 0.3 | ND | 9.7 |
| recovery (%) | 7.4 | 15 | 0.4 | 0.3 | 0.0 | --- |
| 4:45-5:15 mg/L | 117 | 3300 | 7.1 | 0.9 | ND | 10.3 |
| recovery (%) | 7.0 | 13 | 0.3 | 0.7 | 0.0 | --- |

TABLE D-4. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 12)

| Time | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|
| 0:00 mg/L | 164 | 2120 | 259 | 12 | 1.9 | --- |
| 2:30-3:00 mg/L | 120 | 14050 | 14 | 6.1 | 0.40 | 10.5 |
| recovery (%) | 7.0 | 62 | 0.5 | 4.8 | 2.0 | --- |
| 3:00-4:00 mg/L | 146 | 9570 | 9.2 | 12 | ND | 10.7 |
| recovery (%) | 8.3 | 42 | 0.3 | 9.3 | 0.0 | --- |
| 4:00-5:00 mg/L | 123 | 9450 | 7.4 | 9.8 | ND | 11.2 |
| recovery (%) | 6.7 | 40 | 0.3 | 7.3 | 0.0 | --- |

TABLE D-5. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 13)

| Time | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|
| 0:00 mg/L | 165 | 2440 | 238 | 10.2 | 2.2 | --- |
| 2:00 mg/L | 149 | 3930 | 36 | 0.5 | ND | 1.6 |
| recovery (%) | 56 | 100 | 9.5 | 3 | 0.0 | --- |
| 3:30-4:00 mg/L | 131 | 3330 | 28 | 0.3 | ND | 1.7 |
| recovery (%) | 47 | 80 | 69 | 2 | 0.0 | --- |
| 4:00-4:30 mg/L | 137 | 4530 | 28 | 0.4 | ND | 1.8 |
| recovery (%) | 46 | 100+ | 6.5 | 2 | 0.0 | --- |

TABLE D-6. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 14)

| Time | | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|---|
| 0:00 | mg/L | 175 | 2167 | 266 | 11.1 | 2.1 | --- |
| 4:00 | mg/L | 103 | 9370 | 33 | 0.7 | 0.4 | 17.7 |
| | recovery (%) | 3.3 | 24 | 0.7 | 0.4 | 1.1 | --- |
| 5:00 | mg/L | 90 | 9490 | 29 | 3.0 | 1.2 | 11.2 |
| | recovery (%) | 4.6 | 39 | 1.0 | 2.4 | 5.1 | --- |
| 5:30 | mg/L | 103 | 12380 | 13 | ND | ND | 12.8 |
| | recovery | 4.6 | 45 | 0.4 | 0 | 0 | --- |

TABLE D-7. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 15)

| Time | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|
| 0:00 mg/L | 163 | 2350 | 250 | 10.9 | 2.0 | --- |
| 4:30-5:00 mg/L | 132 | 7570 | 28 | 0.8 | 0.5 | 11.1 |
| recovery (%) | 7.3 | 29 | 1.0 | 0.7 | 2.3 | --- |
| 5:00-6:00 mg/L | 138 | 6990 | 53 | 1.3 | 0.4 | 13.9 |
| recovery (%) | 6.1 | 21 | 1.5 | 0.9 | 1.4 | --- |
| 6:00-6:30 mg/L | 162 | 10150 | 31 | 0.8 | 0.3 | 11.2 |
| recovery (%) | 8.9 | 39 | 1.1 | 0.7 | 1.3 | --- |

TABLE D-8. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 16)

| Time | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|
| 0:00 mg/L | 128 | 2480 | 253 | 10.1 | 2.0 | --- |
| 3:00 mg/L | 125 | 5640 | 30 | 1.0 | ND | 10.0 |
| recovery (%) | 9.8 | 23 | 1.2 | 1.0 | 0 | --- |
| 4:00 mg/L | 117 | 6300 | 18 | ND | 2 | 8.5 |
| recovery (%) | 11 | 30 | 0.8 | 0 | 12 | --- |
| 5:00 mg/L | 105 | 7970 | 20 | 4.6 | ND | 9.2 |
| recovery (%) | 8.9 | 35 | 0.9 | 5.0 | 0 | --- |
| 5:30 mg/L | 179 | 8750 | 20 | ND | ND | 10.2 |
| recovery (%) | 14 | 35 | 0.8 | 0 | 0 | --- |

TABLE D-9. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 17)

| Time | Phenol | Hydantoin | Methanol | Acetone | Acetonitrile | Cycles |
|---|---|---|---|---|---|---|
| 0:00 mg/L | 238 | 2380 | 244 | 10.2 | 2.2 | --- |
| 1:00-2:00 mg/L | 359 | 5530 | 21 | 7.4 | 1.7 | 7.4 |
| recovery (%) | 20 | 31 | 1.2 | 9.8 | 10 | --- |
| 2:00-3:00 mg/L | 114 | 6180 | 21 | ND | ND | 10.3 |
| recovery (%) | 4.7 | 25 | 0.8 | 0 | 0 | --- |
| 4:00-5:00 mg/L | 101 | 6130 | 16 | 5.8 | 2.2 | 9.6 |
| recovery (%) | 4.4 | 27 | 0.7 | 5.9 | 10 | --- |
| 5:00-6:00 mg/L | 96 | 7450 | 20 | 0.8 | 0.8 | 8.1 |
| recovery (%) | 5.0 | 39 | 1.0 | 1.0 | 4.5 | --- |
| 6:00-6:51 mg/L | 110 | 9100 | 12 | ND | ND | 7.8 |
| recovery (%) | 5.9 | 49 | 0.6 | 0 | 0 | --- |

TABLE D-10. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 18)

| TIME | PHENOL | HYDANTOIN | METHANOL | ACETONE | ACETONITRILE | CYCLES |
|---|---|---|---|---|---|---|
| 0:00 mg/L | 195 | 7620 | 272 | 29 | 1.9 | -- |
| 2:00 - 3:00 mg/L | 106 | NA | 46 | 30 | 2.3 | 13.7 |
| Recovery (%) | 4.0 | NA | 1.2 | 7.6 | 8.8 | -- |
| 3:00 - 4:00 mg/L | 84 | NA | 39 | 24 | 1.8 | 11.4 |
| Recovery (%) | 3.8 | NA | 1.3 | 7.3 | 8.3 | -- |
| 4:00 - 5:00 mg/L | 84 | 18105 | 47 | 31 | 2.5 | 9.90 |
| Recovery (%) | 4.4 | 24 | 1.7 | 11 | 13.2 | -- |
| 6:11 mg/L | 78 | 37200 | 26 | 43 | 3.3 | 11.9 |
| Recovery | 3.4 | 41 | 0.8 | 12.5 | 14.5 | -- |

TABLE D-11. COOLING TOWER COMPOSITION AND BLOWDOWN RECOVERY (Test 19)

| TIME | | PHENOL | HYDANTOIN | METHANOL | ACETONE | ACETONITRILE | CYCLES |
|---|---|---|---|---|---|---|---|
| 0:00 | mg/L | 244 | 7300 | 230 | 17.4 | 3.0 | -- |
| 4:50 | mg/L | 209 | 23600 | 22 | 18.3 | 2.6 | 8.6 |
| | Recovery (%) | | 38 | 1.1 | 12 | 10 | -- |
| 5:47 | mg/L | 168 | 24000 | 21 | 19.9 | 2.8 | 10.9 |
| | Recovery (%) | | 30 | 0.8 | 10 | 8.5 | -- |
| 6:04 | mg/L | 153 | 23500 | 20 | 28.6 | 3.0 | 10.9 |
| | Recovery (%) | | 30 | 0.8 | 15 | 9.2 | -- |

# APPENDIX E

# MERKEL NUMBER (TOWER CHARACTERISTIC) CALCULATIONS

A sample calculation of Merkel number as explained in Section 3 is given in Table E-1. Enthalpy data have been taken from Appendix B using a linear interpolation between table entries. Calculations for other tests have been made and are given in Table B-2. Tests in the five centimeter tower prior to test 9 were conducted with dry inlet air; calculations for these tests are not presented because they may not be comparable.

## TABLE E-1. SAMPLE CALCULATION FOR TEST 9

TEST 9

$T_1 = 122\ ^{o}F$
$T_2 = 79\ ^{o}F$
$WBT = 68\ ^{o}F$
$L/G = 1.20$ lb/lb

| $T\ ^{o}F$ | $h_w$ | $h_a$ | $h_w-h_a$ | $1/\Delta h$ |
|---|---|---|---|---|
| $T_2 = 79$ | | $h_1 = 32.42$ | | |
| $T_2 + 0.1\ (T_1-T_2) = 83.3$ | 47.39 | $h_1 + 0.1\ (L/G)(T_1-T_2) = 37.58$ | 9.81 | .1019 |
| $T_2 + 0.4\ (T_1-T_2) = 96.2$ | 65.25 | $h_1 + 0.4\ (L/G)(T_1-T_2) = 53.06$ | 12.19 | .0820 |
| $T_1 - 0.4\ (T_1-T_2) = 104.8$ | 80.93 | $h_2 - 0.4\ (L/G)(T_1-T_2) = 63.38$ | 17.55 | .0570 |
| $T_1 - 0.1\ (T_1-T_2) = 117.7$ | 112.58 | $h_2 - 0.1\ (L/G)(T_1-T_2) = 78.86$ | 33.72 | .0297 |
| $T_1 = 122$ | | $h_1 + (L/G)(T_1-T_2) = h_2 = 84.02$ | | |

$\Sigma = .2706$

$$\frac{K_L aV}{L} = \frac{T_1-T_2}{4}\ \Sigma\ \frac{1}{\Delta h} = 2.9$$

## TABLE E-2. MERKEL NUMBER CALCULATION DATA

| Test | Inlet water °F | Outlet water °F | Inlet water wet bulb °F | L/G lb/lb | Merkel No. |
|---|---|---|---|---|---|
| 9 | 122 | 79 | 68 | 1.20 | 2.9 |
| 10 | 122 | 81 | 67 | 1.20 | 2.4 |
| 11 | 122 | 73 | 68 | 0.82 | 4.4 |
| 12 | 142 | 73 | 66 | 0.82 | 3.9 |
| 13 | 122 | 77 | 67 | 1.20 | 3.6 |
| 14 | 122 | 75 | 59 | 1.20 | 2.9 |
| 15 | 122 | 79 | 72 | 1.20 | 4.0 |
| 16 | 122 | 75 | 68 | 1.20 | 5.8 |
| 17 | 122 | 79 | 69 | 1.20 | 3.3 |
| 18 | 122 | 81 | 70 | 1.20 | 2.9 |
| 19 | 122 | 77 | 70 | 1.20 | 4.7 |
| L-1 | 124 | 100 | 69 | 1.60 | 0.52 |
| L-2 | 124 | 100 | 70 | 1.60 | 0.54 |
| L-3 | 109 | 88 | 68 | 0.81 | 0.75 |
| L-4 | 109 | 88 | 69 | 0.81 | 0.78 |
| L-5 | 109 | 88 | 69 | 0.81 | 0.78 |
| L-6 | 124 | 104 | 65 | 2.4 | 0.43 |
| L-7 | 126 | 104 | 65 | 2.4 | 0.44 |
| L-8 | 126 | 102 | 71 | 2.4 | 0.53 |
| L-9 | 126 | 102 | 71 | 1.6 | 0.49 |
| L-10 | 126 | 104 | 65 | 1.6 | 0.38 |
| L-11 | 124 | 102 | 75 | 1.6 | 0.50 |
| L-12 | 122 | 99 | 64 | 1.6 | 0.49 |